DECLARATION

I, Osamu MAEDA, c/o the Inoue & Associates of 3rd Floor, Akasaka Habitation Building, 3-5, Akasaka 1-chome, Minato-ku, Tokyo, Japan do solemnly and sincerely declare that I am conversant with the Japanese and English languages and that I have executed with the best of my ability this translation into English of the Certified Copy of Japanese Patent Application No. 2003-185078 and believe that the translation is true and correct.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

June 18, 2008
_____
(Date)

Osamu Maeda
_____
Osamu MAEDA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of
the following application as filed with this Office.

Date of Application: June 27, 2003

Application Number: Patent Application No. 2003-185078

[ST.10/C]:   [JP2003-185078]

Applicant(s):   Asahi Kasei Chemicals Corporation

June 18, 2004

Yasuo IMAI

Commissioner,

Japan Patent Office

Certif. No. 2004-3052809

[Name of Document] Patent Application

[Reference Number] X1030843

[Date of Application]   June 27, 2003

[Submitted to] Commissioner, Japan Patent Office

[International Patent Classification] C07C 69/017

C07C 68/00

[Inventor]

    [Address]   c/o Asahi Kasei Kabushiki Kaisha,

                3-13-1, Ushiodori,

                Kurashiki-shi, Okayama-ken

    [Name]   Nobuhisa Miyake

[Inventor]

    [Address]   c/o Asahi Kasei Kabushiki Kaisha,

                3-13-1, Ushiodori,

                Kurashiki-shi, Okayama-ken

    [Name]   Kazuhiro Onishi

[Applicant for Patent]

    [Identification Number] 000000033

    [Name]   Asahi Kasei Kabushiki Kaisha

    [Representative]   Shiro Hiruta

[Indication of Fee]

    [Advance Payment Ledger Number] 011187

    [Amount of Advance Payment]   ¥21,000

[List of Materials Being Submitted]

    [Name of Material] Specification 1

    [Name of Material] Abstract   1

[Necessity or Non-Necessity of Proof] Necessary

[Name of Document] Specification

[Title of the Invention] Method for producing an aromatic carbonate

[Scope of Claims for Patent]

[Claim 1] A method for producing an aromatic carbonate, comprising the following steps (1) to (4):

(1) performing a reaction between an organometal compound having a metal-oxygen-carbon linkage and carbon dioxide to obtain a reaction mixture containing a dialkyl carbonate,

(2) separating said dialkyl carbonate from said reaction mixture to obtain a residual liquid,

(3) reacting said residual liquid with an alcohol to form at least one organometal compound having a metal-oxygen-carbon linkage and form water and removing said water from said organometal compound, and

(4) reacting said dialkyl carbonate separated in step (2) with an aromatic hydroxy compound to obtain an aromatic carbonate.

[Claim 2] The method according to claim 1, wherein, in step (3), said organometal compound having said water removed therefrom is recovered.
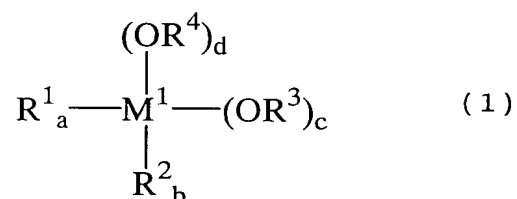
[Claim 3] The method according to claim 1 or 2, wherein, in step (1), said organometal compound is used in an amount

which is 1/200 to 1 time the stoichiometric amount relative to the amount of said carbon dioxide.

[Claim 4] The method according to any one of claims 1 to 3, wherein said reaction in step (1) is performed at 20 °C or higher.

[Claim 5] The method according to any one of claims 1 to 4, wherein said organometal compound used in step (1) comprises at least one compound selected from the group consisting of:

an organometal compound represented by the formula (1):

$$R^1{}_a\!-\!M^1\!\!\begin{matrix}(OR^4)_d \\ | \\ \\ | \\ R^2{}_b\end{matrix}\!\!-\!(OR^3)_c \qquad (1)$$
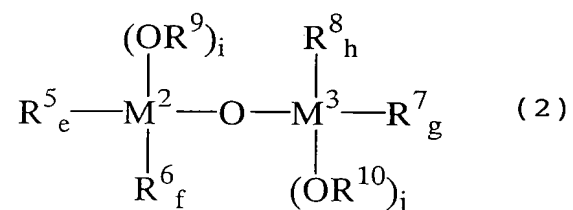
wherein:

M^1 represents a metal atom selected from the group consisting of elements belonging to Groups 4 and 14 of the Periodic Table, exclusive of silicon;

each of R^1 and R^2 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-

C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl, or an unsubstituted or substituted C_6-C_{20} aryl group;

each of R^3 and R^4 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, or a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl; and

each of a and b is an integer of from 0 to 2, a + b = 0 to 2, each of c and d is an integer of from 0 to 4, and a + b + c + d = 4; and

an organometal compound represented by the formula (2):

$$R^5{}_e\!-\!\!\overset{\displaystyle (OR^9)_i}{\underset{\displaystyle R^6{}_f}{\overset{|}{\underset{|}{M^2}}}}\!\!-\!O\!-\!\!\overset{\displaystyle R^8{}_h}{\underset{\displaystyle (OR^{10})_j}{\overset{|}{\underset{|}{M^3}}}}\!\!-\!R^7{}_g \qquad (2)$$

wherein:

each of M^2 and M^3 independently represents a metal atom selected from the group consisting of elements belonging to Groups 4 and 14 of the Periodic Table, exclusive of silicon;

each of R^5, R^6, R^7 and R^8 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl, or an unsubstituted or substituted C_6-C_{20} aryl group;

each of R^9 and R^{10} independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, or a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl; and

each of e, f, g and h is an integer of from 0 to 2, e + f = 0 to 2, g + h = 0 to 2, each of i and j is an

integer of from 1 to 3, $e + f + i = 3$, and $g + h + j = 3$.

[Claim 6] The method according to any one of claims 1 to 5, wherein said separation of said dialkyl carbonate in step (2) is performed by at least one separation method selected from the group consisting of distillation, extraction and filtration.

[Claim 7] The method according to any one of claims 1 to 6, wherein said removal of said water in step (3) is performed by membrane separation.

[Claim 8] The method according to claim 7, wherein said membrane separation is pervaporation.

[Claim 9] The method according to any one of claims 1 to 6, wherein said removal of said water in step (3) is performed by distillation.

[Claim 10] The method according to any one of claims 1 to 9, wherein said alcohol used in step (3) is at least one alcohol selected from the group consisting of an alkyl alcohol having a straight chain or branched C_1-C_{12} alkyl group, a cycloalkyl alcohol having a C_5-C_{12} cycloalkyl group, an alkenyl alcohol having a straight chain or branched C_2-C_{12} alkenyl group, and an aralkyl alcohol having a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl

and alkyl selected from the group consisting of a straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl.

[Claim 11] The method according to any one of claims 1 to 10, wherein said alcohol used in step (3) has a boiling point which is higher than the boiling point of water.

[Claim 12] The method according to claim 11, wherein said alcohol used in step (3) is at least one alcohol selected from the group consisting of n-butyl alcohol, isobutyl alcohol, an alkyl alcohol having a straight chain or branched C_5-C_{12} alkyl group, and an alkenyl alcohol having a straight chain or branched C_4-C_{12} alkenyl group.

[Claim 13] The method according to claim 5, wherein each of R^3 and R^4 in formula (1) and R^9 and R^{10} in formula (2) independently represents an n-butyl group, an isobutyl group, a straight chain or branched C_5-C_{12} alkyl group, or a branched C_4-C_{12} alkenyl group.

[Claim 14] The method according to any one of claims 1 to 13, wherein, in step (1), said organometal compound is used in at least one form selected from the group consisting of a monomeric form, an oligomeric form, a polymeric form and an associated form.

[Claim 15] The method according to claim 5 or 13, wherein each of M^1 in formula (1) and M^2 and M^3 in formula (2)

represents a tin atom.

[Claim 16] The method according to any one of claims 1 to 15, wherein, after step (3), a series of steps (1) to (3) is continuously performed at least one time, wherein step (1) in said series is performed using a reaction mixture obtained by said reaction performed in step (3).

[Claim 17] The method according to any one of claims 1 to 16, wherein said organometal compound used in step (1) is produced from an organotin oxide and an alcohol.

[Claim 18] The method according to any one of claims 1 to 17, wherein the amount of said aromatic hydroxy compound used in step (4) is 1 to 10,000 times the stoichiometric amount relative to the amount of said dialkyl carbonate used in step (4).

[Claim 19] The method according to any one of claims 1 to 18, wherein said reaction in step (4) is performed at a temperature in the range of from 50 to 350 °C.

[Claim 20] The method according to any one of claims 1 to 19, wherein said reaction in step (4) is performed in the presence of a transesterification reaction catalyst.

[Claim 21] The method according to any one of claims 1 to 20, wherein said aromatic hydroxy compound is represented by the following formula (3):

ArOH   (3)

wherein Ar is a C_5-C_{30} aromatic group.

[Claim 22] The method according to any one of claims 1 to 21, wherein said aromatic hydroxy compound is phenol.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a method for producing an aromatic carbonate using carbon dioxide.

[0002]

[Prior Art]

An aromatic carbonate is widely used as carbonyl sources, such as raw materials for producing a polycarbonate, an iso- cyanate and a pharmaceutical, and it has been desired to de- velop a method for producing an aromatic carbonate at a low cost.

As a conventional method for producing an aromatic car- bonate, there can be mentioned a method in which phosgene as a carbonyl source is reacted with an aromatic hydroxy com- pound. However, since this method employs phosgene which is extremely toxic and highly corrosive, the method is disadvan- tageous in that the transportation and storage of phosgene need great care, and the maintenance of production equipment

is costly, which maintenance is indispensable for assuring safety. Further, in the method, hydrochloric acid which is highly corrosive is by-produced in a large amount, thereby causing difficulty in the waste disposal and the like. In view of this, methods which do not employ phosgene have been developed. For example, there has been proposed an oxidative carbonylation method in which an aromatic carbonate is produced from oxygen and an aromatic hydroxy compound using carbon monoxide as a carbonyl source. However, since this method employs carbon monoxide which is extremely toxic, the method is also disadvantageous in that the transportation and handling of carbon monoxide require great care, and the maintenance of the production equipment is costly, which maintenance is indispensable for assuring safety in the production of the aromatic carbonate. Further, the method employs, as a catalyst, palladium which is expensive and difficult to recover. Therefore, the method inevitably becomes an extremely expensive and complicated and, hence, has not been commercialized.

[0003]

As another method for producing an aromatic carbonate, which does not employ phosgene, there has been proposed a method in which urea as a carbonyl source is reacted with an

alcohol to obtain a dialkyl carbonate, and the obtained dial-kyl carbonate is reacted with an aromatic hydroxy compound to obtain an aromatic carbonate. This method is improved in that urea used as a raw material has substantially no toxic-ity. However, in the reaction for producing the dialkyl carbonate from urea and an alcohol, an allophanic ester is inevitably by-produced, thereby lowering the selectivity for the dialkyl carbonate. Therefore, the method for producing an aromatic carbonate using urea as a carbonyl source inevitably becomes costly. Further, an apparatus for the disposal of by-products is also necessary. Therefore, the production of the aromatic carbonate by the method using urea as a carbonyl source inevitably becomes complicated and, hence, the method has not been commercialized.

[0004]

As still another method for producing an aromatic carbonate, which does not employ phosgene, there has been proposed a method in which carbon dioxide as a carbonyl source is reacted with ethylene oxide or the like to obtain a cyclic carbonate, the obtained cyclic carbonate is reacted with an alcohol to obtain a dialkyl carbonate, and the obtained dial-kyl carbonate is reacted with an aromatic hydroxy compound to obtain an aromatic carbonate (see, e.g., patent document 1).

This method is advantageous in that carbon dioxide which has substantially no toxicity and is inexpensive is used as a raw material. However, the method has the following disadvantages. In the method using carbon dioxide as a carbonyl source, carbon dioxide has a low activity and, hence, it is necessary that carbon dioxide be firstly reacted with ethylene oxide having a high activity to thereby obtain a cyclic carbonate. Since there has been known no commercial method for directly producing an aromatic carbonate from the cyclic carbonate and an aromatic hydroxy compound, it is necessary to produce a dialkyl carbonate as an intermediate product. Therefore, the production of an aromatic carbonate by the method inevitably becomes very complicated and costly. Further, when the cost for producing ethylene oxide as a raw material is taken into consideration, the cost for producing an aromatic carbonate by the method is higher. In the method in which ethylene oxide, carbon dioxide and an aromatic hydroxy compound are used as raw materials, ethylene glycol as well as an aromatic carbonate is produced, wherein the theoretical amount of the ethylene glycol is equimolar to the amount of the aromatic carbonate. Therefore, the method is one in which ethylene glycol is co-produced with an aromatic carbonate. Therefore, the method is disadvantageous in that, de-

spite that the amount of ethylene glycol required in the market may be different from the amount of the aromatic carbonate required in the market, the amounts of ethylene glycol and the an aromatic carbonate produced cannot be adjusted to the required amounts.

[0005]

There are known methods in which a carbonic ester is produced using carbon dioxide as a carbonyl source (see patent documents 2, 3 and 4). In these methods, the equilibrium of the reaction is displaced using an organic or inorganic dehydrating agent so as to produce a dialkyl carbonate. When an organic dehydrating agent is used, a large amount of the organic dehydrating agent is denatured by a dehydrating reaction to generate a by-product. Therefore, it becomes necessary to dispose the by-product and regenerate the organic dehydrating agent. For such disposal and regeneration, it is necessary to perform a dehydrating reaction which is difficult to proceed, and a cumbersome separating operation, so that the method inevitably becomes costly. Therefore, the method has not been commercialized. It is also well-known to a skilled person that, when an inorganic dehydrating agent is used instead of an organic dehydrating agent, a large amount of energy is necessary for regenerating the inorganic dehy-

drating agent having absorbed water. Therefore, when a carbonic ester is produced by the method using an organic or inorganic dehydrating agent, it is impossible to produce a carbonic ester at a low cost and, hence, the method has not been commercialized.

As seen from the above, conventional methods for producing an aromatic carbonate by the use, as a carbonyl source, of carbon dioxide which is inexpensive and has substantially no toxicity have problems, such as the generation of a co-product, the generation of a by-product derived from a dehydrating agent, and the disposal of a dehydrating agent.

[0006]

[Patent Document 1]

Unexamined Japanese Patent Application Laid-Open Specification No. Hei 9-40616.

[Patent Document 2]

Unexamined Japanese Patent Application Laid-Open Specification No. 2001-247519

[Patent Document 3]

German Patent No. 4310109

[Patent Document 4]

Unexamined Japanese Patent Application Laid-Open Specification No. 2001-31629

[0007]

[Problems to Be Solved by the Invention]

It is an object of the present invention to provide a commercial method for producing an aromatic carbonate by the use of carbon dioxide having substantially no toxicity as a carbonyl source, without generating a large amount of a co-product or by-product. It is another object of the present invention to provide a commercial method for continuously producing an aromatic carbonate.

[0008]

[Means to Solve the Problems]

The present inventors have made extensive and intensive studies with a view toward solving the above-mentioned problems. As a result, it has been found that an organometal compound can be regenerated by a process in which an organometal compound, carbon dioxide and optionally an alcohol are reacted with one another to obtain a reaction mixture containing a dialkyl carbonate, the dialkyl carbonate is separated from the reaction mixture to obtain a residual liquid comprised mainly of an organometal compound, the residual liquid is reacted with an alcohol, and water produced by the reaction between the residual liquid and the alcohol is removed by distillation or the like. Further, it has also been

found that, since the dialkyl carbonate separated can be subjected to a transesterification reaction with an aromatic hydroxy compound to obtain an aromatic carbonate, it becomes possible to produce only an aromatic carbonate and water from carbon dioxide and an aromatic hydroxy compound as raw materials, wherein substantially no raw materials other than carbon dioxide and the aromatic hydroxy compound are necessary. Based on this finding, the present invention has been completed.

[0009]

That is, the present invention is as follows.

[1] A method for producing an aromatic carbonate, comprising the following steps (1) to (5):

(1) performing a reaction between an organometal compound having a metal-oxygen-carbon linkage and carbon dioxide to obtain a reaction mixture containing a dialkyl carbonate,

(2) separating the dialkyl carbonate from the reaction mixture to obtain a residual liquid,

(3) reacting the residual liquid with an alcohol to form at least one organometal compound having a metal-oxygen-carbon linkage and form water and removing the water from the organometal compound, and

(4) reacting the dialkyl carbonate separated in step (2)

with an aromatic hydroxy compound to obtain an aromatic car-
bonate.

[0010]

[2] The method according to item [1] above, wherein, in
step (3), the organometal compound having the water removed
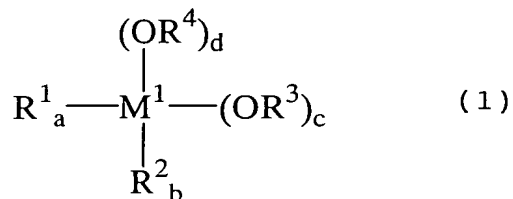therefrom is recovered.

[3] The method according to item [1] or [2] above,
wherein, in step (1), the organometal compound is used in an
amount which is 1/200 to 1 time the stoichiometric amount
relative to the amount of the carbon dioxide.

[4] The method according to any one of items [1] to [3]
above, wherein the reaction in step (1) is performed at 20 °C
or higher.

[5] The method according to any one of items [1] to [4]
above, wherein the organometal compound used in step (1) com-
prises at least one compound selected from the group consist-
ing of:

an organometal compound represented by the formula (1):

[0011]

$$R^1{}_a\!-\!M^1\!\overset{\displaystyle (OR^4)_d}{\underset{\displaystyle R^2{}_b}{\rule[0.5ex]{0pt}{2.5ex}|}}\!-\!(OR^3)_c \qquad (1)$$

[0012]

wherein:

M^1 represents a metal atom selected from the group consisting of elements belonging to Groups 4 and 14 of the Periodic Table, exclusive of silicon;

each of R^1 and R^2 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl, or an unsubstituted or substituted C_6-C_{20} aryl group;
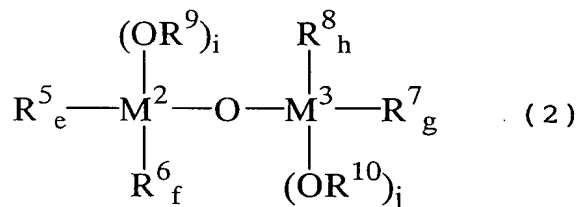
each of R^3 and R^4 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, or a C_7-C_{20} aralkyl group comprised

of unsubstituted or substituted C_6-C_{19} aryl and alkyl

selected from the group consisting of straight chain

or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl; and

each of a and b is an integer of from 0 to 2, a + b

= 0 to 2, each of c and d is an integer of from 0 to 4,

and a + b + c + d = 4; and

an organometal compound represented by the formula (2):

[0013]

$$R^5{}_e\!-\!\underset{\underset{R^6{}_f}{|}}{\overset{\overset{(OR^9)_i}{|}}{M^2}}\!-\!O\!-\!\underset{\underset{(OR^{10})_j}{|}}{\overset{\overset{R^8{}_h}{|}}{M^3}}\!-\!R^7{}_g \qquad (2)$$

[0014]

wherein:

each of M^2 and M^3 independently represents a metal

atom selected from the group consisting of elements

belonging to Groups 4 and 14 of the Periodic Table,

exclusive of silicon;

each of R^5, R^6, R^7 and R^8 independently represents a

straight chain or branched C_1-C_{12} alkyl group, a C_5-

C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl, or an unsubstituted or substituted C_6-C_{20} aryl group;

each of R^9 and R^{10} independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, or a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl; and

each of e, f, g and h is an integer of from 0 to 2, e + f = 0 to 2, g + h = 0 to 2, each of i and j is an integer of from 1 to 3, e + f + i = 3, and g + h + j = 3.

[0015]

[6] The method according to any one of items [1] to [5] above, wherein the separation of the dialkyl carbonate in step (2) is performed by at least one separation method selected from the group consisting of distillation, extraction and filtration.

[7] The method according to any one of items [1] to [6] above, wherein the removal of the water in step (3) is performed by membrane separation.

[8] The method according to item [7] above, wherein the membrane separation is pervaporation.

[9] The method according to any one of items [1] to [6] above, wherein the removal of the water in step (3) is performed by distillation.

[0016]

[10] The method according to any one of items [1] to [9] above, wherein the alcohol used in step (3) is at least one alcohol selected from the group consisting of an alkyl alcohol having a straight chain or branched C_1-C_{12} alkyl group, a cycloalkyl alcohol having a C_5-C_{12} cycloalkyl group, an alkenyl alcohol having a straight chain or branched C_2-C_{12} alkenyl group, and an aralkyl alcohol having a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of a straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl.

[0017]

[11] The method according to any one of items [1] to [10] above, wherein the alcohol used in step (3) has a boiling point which is higher than the boiling point of water.

[12] The method according to item [11] above, wherein the alcohol used in step (3) is at least one alcohol selected from the group consisting of n-butyl alcohol, isobutyl alcohol, an alkyl alcohol having a straight chain or branched C_5-C_{12} alkyl group, and an alkenyl alcohol having a straight chain or branched C_4-C_{12} alkenyl group.

[13] The method according to item [5] above, wherein each of R^3 and R^4 in formula (1) and R^9 and R^{10} in formula (2) independently represents an n-butyl group, an isobutyl group, a straight chain or branched C_5-C_{12} alkyl group, or a branched C_4-C_{12} alkenyl group.

[0018]

[14] The method according to any one of items [1] to [13] above, wherein, in step (1), the organometal compound is used in at least one form selected from the group consisting of a monomeric form, an oligomeric form, a polymeric form and an associated form.

[15] The method according to item [5] or [13] above, wherein each of M^1 in formula (1) and M^2 and M^3 in formula (2) represents a tin atom.

[16] The method according to any one of items [1] to [15] above, wherein, after step (3), a series of steps (1) to (3) is continuously performed at least one time, wherein step

(1) in the series is performed using a reaction mixture obtained by the reaction performed in step (3).

[17]   The method according to any one of items [1] to [16] above, wherein the organometal compound used in step (1) is produced from an organotin oxide and an alcohol.

[0019]

[18]   The method according to any one of items [1] to [17] above, wherein the amount of the aromatic hydroxy compound used in step (4) is 1 to 10,000 times the stoichiometric amount relative to the amount of the dialkyl carbonate used in step (4).

[19]   The method according to any one of items [1] to [18] above, wherein the reaction in step (4) is performed at a temperature in the range of from 50 to 350 °C.

[20]   The method according to any one of items [1] to [19] above, wherein the reaction in step (4) is performed in the presence of a transesterification reaction catalyst.

[21]   The method according to any one of items [1] to [20] above, wherein the aromatic hydroxy compound is represented by the following formula (3):

$$ArOH \qquad\qquad (3)$$
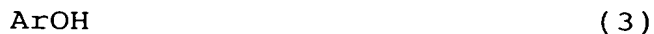
wherein Ar is a C_5-C_{30} aromatic group.

[22]   The method according to any one of items [1] to

[21] above, wherein the aromatic hydroxy compound is phenol.

[0020]
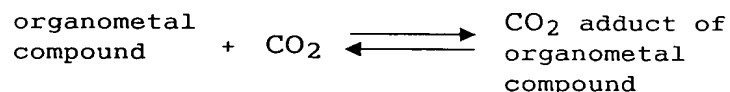
[Mode for Carrying Out the Invention]

The method of the present invention is characterized in that an organometal compound, carbon dioxide and optionally an alcohol are reacted with one another to obtain a reaction mixture containing a dialkyl carbonate, the dialkyl carbonate is separated from the reaction mixture to obtain a residual liquid comprised mainly of a metal-containing component, the residual liquid is reacted with an alcohol to form an organometal compound and water, the water is removed by distillation or the like, and the dialkyl carbonate is reacted with an aromatic hydroxy compound to obtain an aromatic carbonate.
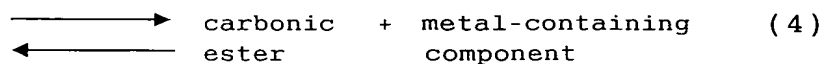
[0021]

Specifically, in step (1) of the method of the present invention, a reaction between an organometal compound and carbon dioxide is performed to form a CO_2 adduct of the organometal compound, followed by a thermal decomposition reaction of the CO_2 adduct, to thereby obtain a reaction mixture containing a dialkyl carbonate (see formula (4) below). In step (2) of the method of the present invention, the dialkyl carbonate is separated from the reaction mixture to obtain a residual liquid containing a metal (see formula (5) below).
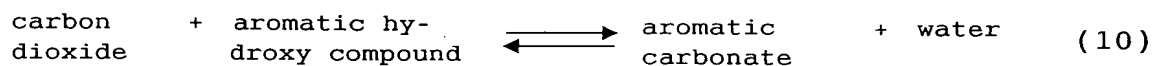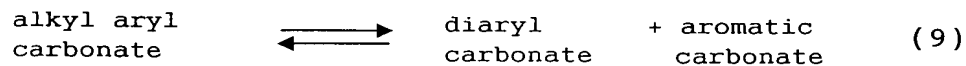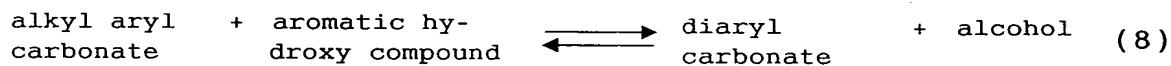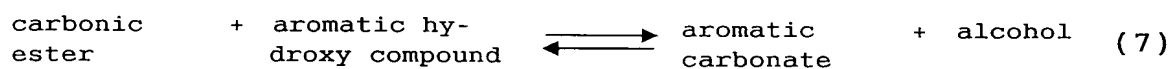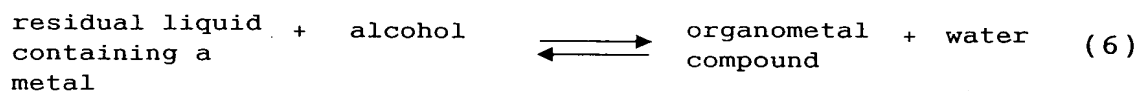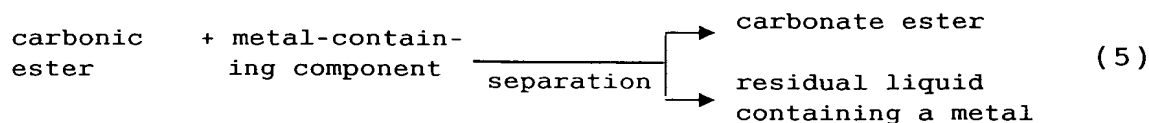
In step (3) of the method of the present invention, the residual liquid containing a metal is reacted with an alcohol to regenerate the organometal compound (see formula (6) below). In step (4) of the method of the present invention, the dialkyl carbonate is reacted with an aromatic hydroxy compound to obtain an aromatic carbonate (see formula (7) below). As an aromatic carbonate, an alkyl aryl carbonate is advantageously obtained. However, it is sometimes possible that an aryl carbonate is obtained by a reaction as shown by formula (8) below. Further, it is also sometimes possible that a diaryl carbonate is obtained by a reaction as shown by formula (9) below, in which an alkyl aryl carbonate is subjected to disproportionation. Therefore, as shown by formula (10) below, the method of the present invention resides in that an aromatic carbonate and water are produced from carbon dioxide and an aromatic hydroxy compound as raw materials.

[0022]

organometal
compound   + CO_2 ⇌ CO_2 adduct of
organometal
compound

thermal
decomposition

⇌   carbonic   +   metal-containing   (4)
ester   component

carbonic + metal-contain-   carbonate ester

ester   ing component   separation   residual liquid   (5)

                                 containing a metal

residual liquid + alcohol   ⇌   organometal + water   (6)
containing a   compound
metal

carbonic + aromatic hy-   ⇌   aromatic + alcohol   (7)
ester   droxy compound   carbonate

alkyl aryl + aromatic hy-   ⇌   diaryl + alcohol   (8)
carbonate   droxy compound   carbonate

alkyl aryl   ⇌   diaryl + aromatic   (9)
carbonate   carbonate   carbonate

carbon + aromatic hy-   ⇌   aromatic + water   (10)
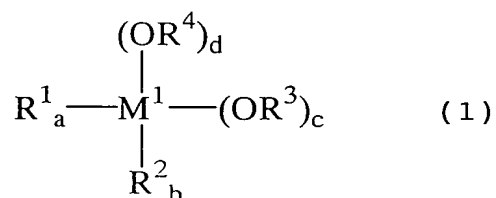dioxide   droxy compound   carbonate

[0023]

The production of the dialkyl carbonate and the separa-

tion of the carbonic ester from the metal-containing compound can be produced by the method described in the present inventors' previous application PCT/JP02/13809.

As an example of the organometal compound having a metal-oxygen-carbon linkage used in step (1) of the method of the present invention, there can be mentioned an organometal compound having an alkoxy group. It is preferred that the organometal compound used in step (1) of the method of the present invention comprises at least one compound selected from the group consisting of:

an organometal compound represented by the formula (1):

[0024]

$$R^1{}_a\!\!-\!\!M^1\!\!\begin{array}{c}(OR^4)_d\\|\\ \!-\!\!(OR^3)_c\\|\\R^2{}_b\end{array}\qquad(1)$$

[0025]

wherein:

M^1 represents a metal atom selected from the group consisting of elements belonging to Groups 4 and 14 of the Periodic Table, exclusive of silicon;
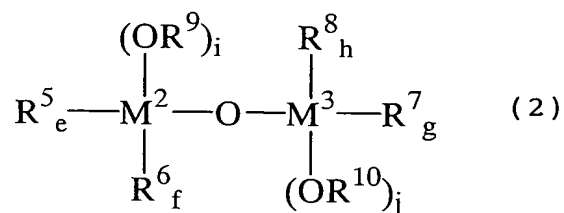
each of R^1 and R^2 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl, or an unsubstituted or substituted C_6-C_{20} aryl group;

each of R^3 and R^4 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, or a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl; and

each of a and b is an integer of from 0 to 2, a + b = 0 to 2, each of c and d is an integer of from 0 to 4, and a + b + c + d = 4; and

an organometal compound represented by the formula (2):
[0026]

$$R^5_e \!\!-\!\! \underset{\underset{R^6_f}{|}}{\overset{\overset{(OR^9)_i}{|}}{M^2}} \!\!-\!\! O \!\!-\!\! \underset{\underset{(OR^{10})_j}{|}}{\overset{\overset{R^8_h}{|}}{M^3}} \!\!-\!\! R^7_g \qquad (2)$$

[0027]

wherein:

each of M^2 and M^3 independently represents a metal atom selected from the group consisting of elements belonging to Groups 4 and 14 of the Periodic Table, exclusive of silicon;

each of R^5, R^6, R^7 and R^8 independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl, or an unsubstituted or substituted C_6-C_{20} aryl group;

each of R^9 and R^{10} independently represents a straight chain or branched C_1-C_{12} alkyl group, a C_5-C_{12} cycloalkyl group, a straight chain or branched C_2-C_{12} alkenyl group, or a C_7-C_{20} aralkyl group comprised

of unsubstituted or substituted C_6-C_{19} aryl and alkyl

selected from the group consisting of straight chain

or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl; and

each of e, f, g and h is an integer of from 0 to 2,

e + f = 0 to 2, g + h = 0 to 2, each of i and j is an

integer of from 1 to 3, e + f + i = 3, and g + h + j =

3.

[0028]

The Periodic Table mentioned herein is as prescribed in

the IUPAC (International Union of Pure and Applied Chemistry)

nomenclature system (1989).

The above-mentioned organometal compound is used in at

least one form selected from the group consisting of a mono-

meric form, an oligomeric form, a polymeric form and an asso-

ciated form.

Each of M^1 in formula (1) and M^2 and M^3 in formula (2)

independently represents a metal atom selected from the group

consisting of elements belonging to Groups 4 and 14 of the

Periodic Table, exclusive of silicon. It is preferred that

each of M^1, M^2 and M^3 is a metal atom selected from the group

consisting of a titanium atom, a tin atom and a zirconium

atom. From the viewpoint of the solubility in and reactivity

with an alcohol, it is more preferred that each of M^1, M^2 and

M^3 is a tin atom.

[0029]

Examples of R^1 and R^2 in formula (1) and R^5, R^6, R^7 and R^8 in formula (2) include C_1-C_{12} alkyl groups and C_5-C_{12} cycloalkyl groups, such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an iso-butyl group, a 2-butenyl group, a pentyl group, a hexyl group, a cyclobutenyl group, a cyclobutyl group, a cyclopentyl group, a cyclopentadienyl group and a cyclohexenyl group; C_7-C_{20} aralkyl groups, such as a benzyl group and a phenylethyl group; and C_6-C_{20} aryl groups, such as a phenyl group, a tolyl group and a naphthyl group. Of the above-mentioned groups, lower alkyl groups are preferred, and straight chain or branched C_1-C_4 alkyl groups are more preferred. Hydrocarbon groups having more carbon atoms than mentioned above can also be used as R^1, R^2, R^5, R^6, R^7 and R^8; however, when such groups having a larger number of carbon atoms are used, there is a danger that the fluidity of the organometal compound and/or the productivity of a diaryl carbonate becomes low.

[0030]

Examples of R^3 and R^4 in the formula (1) and R^9 and R^{10} in the formula (2) include C_1-C_{12} alkyl groups and C_5-C_{12} cycloalkyl groups, such as a methyl group, an ethyl group, an

n-propyl group, an isopropyl group, an n-butyl group, an iso-butyl group, a 2-butenyl group, a pentyl group, a hexyl group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclopentadienyl group, a cyclohexyl group, a cyclohexenyl group, a methoxyethyl group and an ethoxymethyl group; and C_7-C_{20} aralkyl groups, such as a benzyl group and a phenylethyl group.

[0031]

Specific examples of organometal compounds represented by formula (1) above include tetramethoxytin, tetraethoxytin, tetrapropyloxytin, tetrabutyloxytin, tetrapentyloxytin, tetrahexyloxytin, tetrakis(2-ethyl-1-hexyloxy)tin, dimethoxydiethoxytin, tetramethoxytitanium, tetraethoxytitanium, tetrapropyloxytitanium, tetraisopropyloxytitanium, tetrakis(2-ethyl-1-hexyloxy)titanium, dimethyldimethoxytin, dimethyldiethoxytin, dimethylmethoxy(2-ethyl-1-hexyloxy)tin, dimethyldipropyloxytin, dimethyldibutyloxytin, dimethyldi(2-ethyl-1-butyloxy)tin, dimethyldipentyloxytin, dimethyldihexyloxytin, dimethyldicyclohexyloxytin, dimethyldi(2-ethyl-1-hexyloxy)tin, dimethyldipropenyloxytin, dimethyldibenzyloxytin, methylbutyltin dimethoxide, methylbutyltin diethoxide, methylbutylmethoxy(2-ethyl-1-hexyloxy)tin, methylbutyltin dipropoxide, methylbutyltin dibutoxide, methylbu-

tyldi(2-ethyl-1-butoxy)tin, methylbutyltin dipentyloxide, me-
thylbutyltin dihexyloxide, methylbutyltin dicyclohexyloxide,
methylbutyldi(2-ethyl-1-hexyloxy)tin, methylbutyltin dipro-
penyloxide, methylbutyltin dibenzyloxide, methyl(2-ethyl-1-
hexyl)tin dimethoxide, methyl(2-ethyl-1-hexyl)tin diethoxide,
methylmethoxy(2-ethyl-1-hexyl)(2-ethyl-1-hexyloxy)tin,
methyl(2-ethyl-1-hexyl)tin dipropoxide, methyl(2-ethyl-1-
hexyl)tin dibutoxide, methyl(2-ethyl-1-hexyl)tin di(2-ethyl-
1-butoxide), methyl(2-ethyl-1-hexyl)tin dipentyloxide,
methyl(2-ethyl-1-hexyl)tin dihexyloxide, methyl(2-ethyl-1-
hexyl)tin dicyclohexyloxide, methyl(2-ethyl-1-hexyl)tin di(2-
ethyl-1-hexyloxide), methyl(2-ethyl-1-hexyl)tin dipropenylox-
ide, methyl(2-ethyl-1-hexyl)tin dibenzyloxide, butyl(2-ethyl-
1-hexyl)tin dimethoxide, butyl(2-ethyl-1-hexyl)tin diethoxide,
butylmethoxy(2-ethyl-1-hexyl)(2-ethyl-1-hexyloxy)tin, bu-
tyl(2-ethyl-1-hexyl)tin dipropoxide, butylbutoxy(2-ethyl-1-
hexyl)tin, butyl(2-ethyl-1-hexyl)tin di(2-ethyl-1-butoxide),
butyl(2-ethyl-1-hexyl)tin dipentyloxide, butyl(2-ethyl-1-
hexyl)tin dihexyloxide, butyl(2-ethyl-1-hexyl)tin dicyclo-
hexyloxide, butyl(2-ethyl-1-hexyl)tin di(2-ethyl-1-
hexyloxide), butyl(2-ethyl-1-hexyl)tin dipropenyloxide, bu-
tyl(2-ethyl-1-hexyl)tin dibenzyloxide, di-n-butyltin dimeth-
oxide, di-n-butyltin diethoxide, di(n-butyl)methoxy(2-ethyl-

1-hexyloxy)tin, di-n-butyltin dipropoxide, di-n-butyltin dibutoxide, di-n-butyltin di(2-ethyl-1-butoxide), di-n-butyltin dipentyloxide, di-n-butyltin dihexyloxide, di-n-butyltin dicyclohexyloxide, di-n-butyltin di(2-ethyl-1-hexyloxide), di-n-butyltin dipropenyloxide, di-n-butyltin dibenzyloxide, di-t-butyltin dimethoxide, di-t-butyltin diethoxide, di(t-butyl)methoxy(2-ethyl-1-hexyloxy)tin, di-t-butyltin dipropoxide, di-t-butyltin dibutoxide, di-t-butyltin di(2-ethyl-1-butoxide), di-t-butyltin dipentyloxide, di-t-butyltin dihexyloxide, di-t-butyltin dicyclohexyloxide, di-t-butyltin di(2-ethyl-1-hexyloxide), di-t-butyltin dipropenyloxide, di-t-butyltin dibenzyloxide, diphenyltin dimethoxide, diphenyltin diethoxide, diphenylmethoxy(2-ethyl-1-hexyloxy)tin, diphenyltin dipropoxide, diphenyltin dibutoxide, diphenyltin di(2-ethyl-1-butoxide), diphenyltin dipentyloxide, diphenyltin dihexyloxide, diphenyltin dicyclohexyloxide, diphenyltin di(2-ethyl-1-hexyloxide), diphenyltin dipropenyloxide and diphenyltin dibenzyloxide.

[0032]

Examples of organometal compounds represented by formula (2) above include alkoxydistannoxanes and aralkyloxydistannoxanes, such as 1,1,3,3-tetrabutyl-1,3-dimethoxydistannoxane, 1,1,3,3-tetrabutyl-1-methoxy-3-(2-ethyl-1-hexyloxy)-

distannoxane, 1,1,3,3-tetrabutyl-1,3-diethoxydistannoxane,

1,1,3,3-tetrabutyl-1,3-dipropyloxydistannoxane,

1,1,3,3-tetrabutyl-1,3-dibutyloxydistannoxane,

1,1,3,3-tetrabutyl-1,3-dipentyloxydistannoxane,

1,1,3,3-tetrabutyl-1,3-dihexyldistannoxane,

1,1,3,3-tetrabutyl-1,3-di(2-ethyl-1-hexyloxy)-distannoxane,

1,1,3,3-tetrabutyl-1,3-di(2-ethyl-1-butyloxy)-distannoxane,

1,1,3,3-tetrabutyl-1,3-dicyclohexyloxydistannoxane,

1,1,3,3-tetraphenyl-1,3-dimethoxydistannoxane,

1,1,3,3-tetraphenyl-1-methoxy-3-(2-ethyl-1-hexyloxy)-

distannoxane, 1,1,3,3-tetraphenyl-1,3-diethoxydistannoxane,

1,1,3,3-tetraphenyl-1,3-dipropyloxydistannoxane,

1,1,3,3-tetraphenyl-1,3-dibutyloxydistannoxane,

1,1,3,3-tetraphenyl-1,3-dipentyloxydistannoxane,

1,1,3,3-tetraphenyl-1,3-dihexydistannoxane,

1,1,3,3-tetraphenyl-1,3-di(2-ethyl-1-hexyloxy)-distannoxane,

1,1,3,3-tetraphenyl-1,3-di(2-ethyl-1-butyloxy)-distannoxane,

and 1,1,3,3-tetraphenyl-1,3-dicyclohexyloxydistannoxane.

[0033]

The above-mentioned organometal compounds can be used individually or in combination. Further, an orgnometal com-pound other than mentioned above can be used in combination with any of the above-mentioned organometal compounds. As an

organometal compound, those which are commercially available can be used. Alternatively, an organometal compound can be produced by a conventional method. For example, an organometal compound can be produced by a method described in Dutch Patent No. 6612421, in which dibutyltin oxide is reacted with an alcohol having four or more carbon atoms in an azeotropic solvent, and an organometal compound of formula (1) above is obtained as a distillate. Dutch Patent No. 6612421 states that an organometal compound having an alkoxy group having less than four carbon atoms cannot be produced by the method described therein, and that such an organometal compound can be produced from dichlorodibutyltin and a sodium alcoholate. Further, as organometal compounds of formulae (1) and (2) above, there can be used those which are obtained by the method described in the present inventors' previous application PCT/JP02/13809, in which such organometal compounds are produced from a metal oxide and an alcohol. By this method, there can be obtained an organometal compound having an alkoxy group having three or less carbon atoms (such as a methoxy group). For example, an organometal compound having a methoxy group can be obtained from dibutyltin oxide, methanol and hexane. It is conventionally known that methanol and hexane forms a minimum azeotropic mixture; however, it has

surprisingly been found by the present inventors that an organometal compound can be obtained using an alcohol having a boiling point lower than that of water. In the method described in PCT/JP02/13809, the organometal compound obtained from dibutyltin oxide and an alcohol having a boiling point lower than that of water tends to be comprised mainly of an organometal compound of formula (2). However, if desired, a large amount of an organometal compound of formula (1) can be obtained by subjecting the above-mentioned organometal compound comprised mainly of an organometal compound of formula (2) to distillation, thereby obtaining an organometal compound of formula (1) as a distillate.

[0034]

The organometal compounds which are, respectively, represented by formulae (1) and (2) can be identified by ^{119}Sn-NMR spectroscopy (see, for example, U.S. Patent No. 5,545,600). However, it is known that, in a ^{119}Sn-NMR spectrum, the value of a chemical shift ascribed to the structure of the organometal compound represented by formula (1) largely varies depending, for example, on the organometal compound content of the sample used for a ^{119}Sn-NMR analysis and on the presence or absence of an alcohol in the sample used for a ^{119}Sn-NMR analysis. Therefore, it is preferred

that the analysis of the organometal compound is performed by a method in which ^{1}H-NMR spectroscopy and ^{13}C-NMR spectroscopy are used in combination with the above-mentioned ^{119}Sn-NMR spectroscopy.

[0035]

In step (1) of the method of the present invention, an organometal compound having a metal-oxygen-carbon linkage is reacted with carbon dioxide to form a CO_2 adduct of the organometal compound, followed by a thermal decomposition reaction of the CO_2 adduct, to thereby obtain a dialkyl carbonate.

Since step (1) is a step in which a dialkyl carbonate is obtained from a metal alkoxide and carbon dioxide, the use of an alcohol in step (1) is optional. However, by the use of an alcohol, it sometimes becomes possible to obtain a dialkyl carbonate in high yield. The reason for this is as follows. The reaction in step (1) has a reverse reaction. By adding an alcohol to the reaction system, it becomes possible to suppress the advance of the reverse reaction. When the alcohol added to the reaction system contains a large amount of water, the yield of the dialkyl carbonate is lowered. Therefore, it is preferred that the amount of water contained in the alcohol is not more than 0.1 time, more advantageously not more than 0.01 time, the stoichiometric amount relative

to the amount of the metal atom contained in the organometal compound. As the alcohol, a part of the alcohol used for producing an organometal compound can be used. More specific explanation is given below. An alcohol is used for producing at least one organometal compound selected from the group consisting of an organometal compound of formula (1) and an organometal compound of (2) used in step (1), and water generated is removed by distillation, wherein the distillation is stopped when a part of the alcohol which remains unreacted still remains unvaporized. The alcohol remaining unvaporized can be used in step (1) as at least a part of the alcohol.

The temperature for the reaction in step (1) is generally from 20 °C (room temperature) to 300 °C. For completing the reaction in a short period of time, it is preferred to perform the reaction at 80 to 200 °C for 10 minutes to 500 hours.

[0036]

In step (1), carbon dioxide can be used in an amount which is 1 to 200 times the stoichiometric amount relative to the amount of the organometal compound having a metal-oxygen-carbon linkage. When an alcohol is used in step (1) and a largely excess amount of carbon dioxide is present in the reaction system in step (1), the equilibrium of the reaction in

step (1) is further displaced in the direction of the desired

product formation to produce free water. Therefore, it is

preferred that carbon dioxide is used in an amount which is 1

to 50 times the stoichiometric amount relative to the amount

of the organometal compound. Further, when the amount of

carbon dioxide is large, the reaction in step (1) becomes a

high pressure reaction so that not only does it become neces-

sary to use a reaction vessel having high pressure resistance,

but also a large amount of carbon dioxide is wasted during

purging of unreacted carbon dioxide after completion of step

(1). Therefore, it is more preferred that carbon dioxide is

used in an amount which is 1 to 20 times the stoichiometric

amount relative to the amount of the organometal compound.

Thus, in step (1), the amount of carbon dioxide is 1/200 to 1

time, preferably 1/50 to 1 time, more preferably 1/20 to 1

time, as large as the stoichiometric amount relative to the

amount of the organometal compound. When the reaction in

step (1) is performed at room temperature (20 °C) or higher,

the solubility of carbon dioxide in the alcohol is limited

and, therefore, there is a danger that the reaction rate be-

comes extremely low. Accordingly, the pressure employed for

the reaction in step (1) is generally from atmospheric pres-

sure to 200 MPa, preferably from atmospheric pressure to 100

MPa, wherein, if desired, the reaction may be performed while introducing additional carbon dioxide into the reaction system. The introduction of additional carbon dioxide into the reaction system may be performed intermittently or continuously.

When it is confirmed by the analysis of the obtained reaction mixture (which is a liquid) that a satisfactory amount of the desired dialkyl carbonate has been obtained, step (1) is stopped. For example, when the dialkyl carbonate is obtained in an amount which is 10 % or more, based on the stoichiometric amount relative to the amount of the organometal compound, the reaction mixture may be taken out from the reaction vessel after the pressure in the reaction vessel is reduced to atmospheric pressure or, alternatively, without reducing the pressure in the reaction vessel.

[0037]

In the method of the present invention, an alcohol is also used in step (3). Hereinafter, the alcohol used in step (3) is referred to as a "first alcohol", and the alcohol used in step (1) is referred to as a "second alcohol". The first and second alcohols may be the same or different from each other. Examples of such alcohols include alkyl alcohols having a straight chain or branched C_1-C_{12} alkyl group, cycloal-

kyl alcohols having a C_5-C_{12} cycloalkyl group, alkenyl alcohols having a straight chain or branched C_2-C_{12} alkenyl group, and aralkyl alcohols having a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl. Specific examples of these alcohols include C_1-C_{12} aliphatic alcohols and C_5-C_{12} alicyclic alcohols, such as methanol, ethanol, propanol, 2-propanol, n-butyl alcohol, t-butyl alcohol, isobutyl alcohol, 2-butanol, pentanol (and isomers thereof), hexanol (and isomers thereof), 2-ethyl-1-hexanol, nonanol (and isomers thereof), decanol (and isomers thereof), undecanol (and isomers thereof), hexenol (and isomers thereof), cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol and cyclohexenol; and aralkyl alcohols, such as benzyl alcohol and phenethyl alcohol. Further, polyhydric alcohols may be used. Examples of polyhydric alcohols include polyhyric C_1-C_{12} aliphatic alcohols and polyhydric C_5-C_{12} alicyclic alcohols, such as ethylene glycol, 1,3-propanediol, 1,2-propanediol, cyclohexanediol and cyclopentanediol; and aralkyl alcohols, such as benzenedimethanol.

[0038]

Among the above-mentioned alcohols, preferred are those

which have a boiling point higher than that of water, such as alkyl alcohols, cycloalkyl alcohols, alkenyl alcohols and aralkyl alcohols, since, in the regeneration of an organometal compound in step (3), water can be easily distilled off. Specific examples of preferred alkyl alcohols include n-butyl alcohol, isobutyl alcohol, and an alkyl alcohol having a straight chain or branched C_5-C_{12} alkyl group. Specific examples of preferred alkenyl alcohols include those which have a straight chain or branched C_4-C_{12} alkenyl group.

[0039]

Specific examples of preferred alcohols include isobutyl alcohol, pentanol (and isomers thereof), hexanol (and isomers thereof), 2-ethyl-1-hexanol, nonanol (and isomers thereof), decanol (and isomers thereof), undecanol (and isomers thereof), dodecanol (and isomers thereof), hexenol, cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol and cyclohexenol.

[0040]

In the method of the present invention, the reaction system in step (1) may contain substances other than mentioned above. Examples of other substances which are useful in step (1) include those which function as a dehydrating agent in the reaction system. By using a dehydrating agent

in step (1), the reaction system can be maintained non-aqueous. As a dehydrating agent, any conventional organic dehydrating agent may be used. Examples of dehydrating agents include acetal compounds and orthoesters, such as orthotrimethyl acetate. Further, dicyclohexylcarbodiimide and the like may also be used as an organic dehydrating agent. Alternatively, solid dehydrating agents, such as molecular sieves, may be used as a dehydrating agent. When a solid dehydrating agent is used, it is preferred that the solid dehydrating agent is removed from the reaction system before step (3) is performed.

[0041]

In step (1), the use of an alcohol is optional. From the viewpoint of improving the purity of the dialkyl carbonate, as the second alcohol, it is preferred to use an alcohol having an organic group which is the same as an alkoxy group or aralkyloxy group of the organometal compound. When such an alcohol is used as the second alcohol, it is preferred that the amount of the second alcohol is 1 to 100,000 times the stoichiometric amount relative to the amount of the organometal compound. On the other hand, when an alcohol having an organic group different from an alkoxy group or an aralkyloxy group of the organometal compound is used as the second alco-

hol or when, as the organometal compound, only an organometal compound of formula (2) is used, the amount of the second alcohol is preferably 2 to 1,000 times, more preferably 10 to 1,000 times, as large as the stoichiometric amount relative to the amount of the organometal compound. When an alcohol having an organic group different from an alkoxy group or an aralkyloxy group of the organometal compound is used as the second alcohol, an asymmetric dialkyl carbonate is produced in step (1).

[0042]

When an organometal compound formed in step (3) is recycled to step (1), the organometal compound may be recycled together with the unreacted alcohol as the above-mentioned second alcohol so that the amount of the second alcohol falls within the above-mentioned range. Alternatively, the organometal compound may be separated from the unreacted alcohol and, then, recycled to step (1).

In step (2), the dialkyl carbonate is separated from the reaction mixture obtained in step (1). The separation of the dialkyl carbonate in step (2) can be performed by a conventional separation method. Examples of such separation methods include extraction, distillation, filtration and membrane separation. As a preferred solvent for extraction, there can

be mentioned a solvent which does not react with a dialkyl carbonate. Examples of such preferred solvents include aliphatic hydrocarbons, such as hexane and cyclohexane; halogenated hydrocarbons, such as chloroform, dichloromethane and trichloromethylene; aromatic hydrocarbons, such as benzene, toluene and chlorobenzene; and ethers, such as diethyl ether and anisole.

[0043]

In step (1), when methanol and/or ethanol is used as a second alcohol, or when a second alcohol is not used and the organometal compound has a methoxy group and/or ethoxy group, it is possible to obtain a reaction mixture containing a dialkyl carbonate (such as dimethyl carbonate or diethyl carbonate) having a boiling point of 100 °C or lower (wherein the boiling point is measured under atmospheric pressure). Such a dialkyl carbonate can be separated directly from the reaction mixture by distillation. The distillation can be performed by any of conventionally employed distillation methods, such as a distillation under atmospheric pressure, a distillation under reduced pressure and a distillation under superatmospheric pressure. The temperature for the distillation is generally from -20 °C to the boiling point of the dialkyl carbonate, preferably from 20 °C to the boiling point

of the dialkyl carbonate. The distillation may be performed
in the presence of a solvent or by extractive distillation.
On the other hand, when the dialkyl carbonate has a boiling
point higher than 100 °C (wherein the boiling point is meas-
ured under atmospheric pressure) or has six or more carbon
atoms so that the boiling point of the dialkyl carbonate is
high, the reverse reaction in the equilibrium reaction of the
above-mentioned formula (4) is greatly promoted, thereby low-
ering the yield of the dialkyl carbonate. In such a case, a
distillation is performed under highly reduced pressure.

The reaction mixture obtained in step (1) may contain
the organometal compound remaining unreacted and a thermal
decomposition product of the organometal compound. Step (2)
may be performed after or while removing the organometal com-
pound remaining unreacted and the thermal decomposition prod-
uct from the reaction mixture obtained in step (1).

[0044]

In step (2), even the dialkyl carbonate having a boiling
point higher than 100 °C can be easily separated by a method
in which water or a water-containing solvent is added to the
reaction mixture obtained in step (1) to form a white slurry,
solids in the white slurry are removed by filtration to ob-
tain a filtrate, and the obtained filtrate is subjected to

distillation. With respect to the water used in this method, there is no particular limitation; however, it is preferred to use a distilled water or a deionized water.

In step (2), the temperature at which water is added to the reaction mixture obtained in step (1) is in the range from a temperature (e.g., -20 °C) at which the water is not frozen in the reaction mixture to 100 °C. After completion of step (1), it is preferred that the temperature of the reaction mixture may be adjusted to 10 to 80 °C. When the dialkyl carbonate formed in step (1) is susceptible to hydrolysis, for satisfactorily suppressing the occurrence of the hydrolysis of the dialkyl carbonate, it is more preferred to adjust the temperature of the reaction mixture to 10 to 50 °C. When water is used in step (2), water may be used alone or in combination with a solvent other than water. As a solvent other than water, any of those which do not react with the dialkyl carbonate can be used. In this case, when water is used in the form of a solution thereof in an alcohol which is the same as used in step (1), the separation of the solvent by the distillation becomes easy.

[0045]

As a method for distillation, there can be mentioned a distillation method which is conventionally known in the art,

such as distillation under atmospheric pressure, distillation under reduced pressure and distillation under superatmospheric pressure. The distillation can be performed at a temperature of from -20 °C to the boiling point of the dialkyl carbonate and/or the alcohol, preferably from 50 °C to the boiling point of the dialkyl carbonate and/or the alcohol. The distillation may be performed in the presence of another solvent or by extractive distillation.

The dialkyl carbonate contained in the reaction mixture obtained in step (1) may be separated also by a method in which water and/or an extraction solvent is added to the reaction mixture obtained in step (1) to obtain a mixture containing an oil phase containing the dialkyl carbonate, followed by recovery of the dialkyl carbonate from the mixture.

[0046]

In step (3), an organometal compound is synthesized. Step (3) can be performed by the method described in the present inventors' previous application PCT/JP02/13809. The residual liquid obtained in step (2) after the separation of the dialkyl carbonate contains a metal. The residual liquid is generally obtained in the form of a transparent liquid. However, in the residual liquid, the metal is sometimes present in the form of solids. Even in this case, an organome-

tal compound can be synthesized from the residual liquid in step (3).

In step (3), the residual liquid which is obtained in step (2) after separation of the dialkyl carbonate and which contains a metal-containing component is reacted with an alcohol to form an organometal compound (which can be used in step (1)) and water and, then, the water is removed from the organometal compound. If desired, the organometal compound is recovered.

[0047]

Examples of first alcohols used in step (3) include alkyl alcohols having a straight chain or branched C_1-C_{12} alkyl group, cycloalkyl alcohols having a C_5-C_{12} cycloalkyl group, alkenyl alcohols having a straight chain or branched C_2-C_{12} alkenyl group, and aralkyl alcohols having a C_7-C_{20} aralkyl group comprised of unsubstituted or substituted C_6-C_{19} aryl and alkyl selected from the group consisting of straight chain or branched C_1-C_{14} alkyl and C_5-C_{14} cycloalkyl. Specific examples of these alcohols include C_1-C_{12} aliphatic alcohols and C_5-C_{12} alicyclic alcohols, such as methanol, ethanol, propanol, 2-propanol, n-butyl alcohol, t-butyl alcohol, isobutyl alcohol, 2-butanol, pentanol (and isomers thereof), hexanol (and isomers thereof), 2-ethyl-1-hexanol, nonanol

(and isomers thereof), decanol (and isomers thereof), undeca-
nol (and isomers thereof), hexenol (and isomers thereof),
cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol and
cyclohexenol; and aralkyl alcohols, such as benzyl alcohol
and phenethyl alcohol. Further, polyhydric alcohols may be
used. Examples of polyhydric alcohols include polyhyric C_1-
C_{12} aliphatic alcohols and polyhydric C_5-C_{12} alicyclic alco-
hols, such as ethylene glycol, 1,3-propanediol, 1,2-
propanediol, cyclohexanediol and cyclopentanediol; and aral-
kyl alcohols, such as benzenedimethanol.

[0048]

Among the above-mentioned alcohols, preferred are those
which have a boiling point higher than that of water, such as
alkyl alcohols, cycloalkyl alcohols, alkenyl alcohols and
aralkyl alcohols, since, in the regeneration of an organome-
tal compound in step (3), water can be easily distilled off.
Specific examples of preferred alkyl alcohols include n-butyl
alcohol, isobutyl alcohol, and an alkyl alcohol having a
straight chain or branched C_5-C_{12} alkyl group. Specific ex-
amples of preferred alkenyl alcohols include those which have
a straight chain or branched C_4-C_{12} alkenyl group.

[0049]

Specific examples of preferred first alcohols used in

step (3) include isobutyl alcohol, pentanol (and isomers thereof), hexanol (and isomers thereof), 2-ethyl-1-hexanol, nonanol (and isomers thereof), decanol (and isomers thereof), undecanol (and isomers thereof), dodecanol (and isomers thereof), hexenol, cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol and cyclohexenol.

[0050]

If desired, the first alcohol used in step (3) may, prior to use thereof, be subjected to distillation or the like for the purification thereof or the adjustment of the concentration thereof. In view of this, it is preferred to use, as the first alcohol, an alcohol having a boiling point (as measured under atmospheric pressure) of 300 °C or lower.

When a polyhydric alcohol is used as the first alcohol in step (3), it is possible that the organometal compound (metal alkoxide or metal aralkoxide) is obtained in the form of a crosslinked product of an organometal compound of formula (1) or (2) in step (3). Even such a crosslinked product can be used in the present invention.

In step (3), the amount of the first alcohol is preferably 1 to 10,000 times, more preferably 2 to 100 times, as large as the stoichiometric amount relative to the amount of the metal atom contained in the organometal compound used in

step (1).

The temperature for the reaction in step (3) varies depending on the type of the alcohol used in step (3); however, the reaction in step (3) is generally performed at room temperature (20 °C) to 300 °C.

[0051]

The removal of water in step (3) can be performed by any conventional dehydration method which is generally employed in the art. The removal of water may be performed by, for example, the use of dehydration column packed with a solid dehydrating agent (e.g., molecular sieves), distillation, or membrane separation. However, when it is intended to obtain a large amount of an organometal compound within a short period of time, it is preferred that the removal of water is performed by distillation (the use of a solid dehydrating agent has a disadvantage in that the regeneration of a solid dehydrating agent is cumbersome). The distillation may be performed by any conventional distillation method, such as a distillation under atmospheric pressure, a distillation under reduced pressure, a distillation under superatmospheric pressure, thin film distillation or extractive distillation. The distillation can be performed at a temperature of from -20 °C to the boiling point of the first alcohol used in step (3),

preferably from 50 °C to the boiling point of the first alcohol. The removal of water may be performed while adding another substance. When an alcohol having a boiling point higher than that of water is used as the first alcohol, water can be removed by distilling off the water. When the removal of water is performed by membrane separation, for efficiently removing water, it is preferred that the removal of water is performed by pervaporation.

[0052]

When the removal of water in step (3) is performed by distillation, the distillation temperature is not particularly limited so long as the distillation temperature is equal to or lower than the boiling point of the first alcohol and is a temperature at which water has a vapor pressure. When it is intended to complete the distillation within a short period of time, it is preferred that the distillation is performed at the azeotropic temperature of a mixture of water and the first alcohol. When water and the first alcohol do not form an azeotropic mixture, it is preferred that the distillation is performed at the boiling point of water.

Further, even when the first alcohol does not form an azeotropic mixture with water, water can be removed by an azeotropic distillation in which a solvent forming an

azeotropic mixture with water is used. This method is pre-
ferred since water can be removed at a relatively low tem-
perature. Examples of solvents which form an azeotropic mix-
ture with water include unsaturated and saturated hydrocar-
bons, such as hexane, benzene, toluene, xylene and naphtha-
lene; ethers, such as anisole and 1,4-dioxane; hydrogenated
hydrocarbons, such as chloroform.

[0053]

From the viewpoint of facilitating the separation of wa-
ter from the azeotropic mixture after azeotropic distillation,
it is preferred to use, as the above-mentioned solvent used
for forming an azeotropic mixture, an unsaturated or satu-
rated hydrocarbon in which water has a low solubility. When
such a solvent is used, it is necessary to use the solvent in
an amount such that water can be satisfactorily removed by
azeotropic distillation. It is preferred to use a distilla-
tion column for the azeotropic distillation because the sol-
vent can be recycled to the reaction system after separating
the solvent from the azeotropic mixture in the distillation
column and, hence, azeotropic distillation can be performed
using only a relatively small amount of the solvent.

[0054]

By the reaction in step (3), there can be obtained at

least one organometal compound selected from the group consisting of the organometal compounds represented by formulae (1) and (2).

When it is confirmed that the formation of water has almost stopped, step (3) can be stopped. When the reaction mixture (obtained in step (3)) containing an organometal compound and water is recycled to step (1), the yield of a dialkyl carbonate in step (1) varies depending on the amount of water in the reaction mixture. Therefore, it is preferred that water in the reaction mixture obtained in step (3) is removed as much as possible.

Generally, the amount of water removed in step (3) is in the range of from 0.01 to 1 time the amount of water produced by the reaction in step (3), wherein the amount of the produced water is theoretically calculated on the assumption that only a metal alkoxide or metal aralkoxide represented by the above-mentioned formula (1) is produced by the reaction in step (3).

[0055]

After completion of step (3), if desired, an excess amount of the first alcohol may be removed. From the viewpoint of improving the purity of the dialkyl carbonate in the case where the reaction mixture obtained in step (3) is recy-

cled to step (1), it is preferred to remove an excess amount of the first alcohol. When the same alcohol as the first alcohol used in step (3) is used as the second alcohol in step (1), it is not necessary to remove an excess amount of the first alcohol and, if desired, an appropriate amount of the alcohol may be added to the reaction mixture after completion of step (3). If desired, the organometal compound obtained in step (3) is recycled to step (1).

[0056]

When, in step (3), the metal alkoxide or metal aralkoxide is obtained in a solid form, the removal of an excess amount of the first alcohol can be performed by filtration. On the other hand, when the metal alkoxide or metal aralkoxide is obtained in a liquid form, the removal of an excess amount of the first alcohol can be performed by a distillation under reduced pressure, or by a method in which an inert gas, such as nitrogen, is introduced into the reaction vessel used in step (3) to remove at least a part of the first alcohol present in a vapor form. When the removal of an excess amount of the first alcohol is performed by the method using an inert gas, it is necessary to use, as the inert gas, a satisfactorily dried gas. Otherwise, the metal alkoxide or metal aralkoxide is inevitably hydrolyzed in the presence of

water contained in the inert gas to thereby form a metal oxide and an alcohol. Therefore, the yield of a dialkyl obtained in step (1) in the case where the reaction mixture obtained in step (3) is recycled to step (1) is lowered.

In recycling to step (1) the organometal compound having water removed therefrom, the organometal compound may be cooled or heated before the recycling thereof to step (1). Recycling of the organometal compound may be performed in a continuous or batchwise manner. If desired, in addition to the organometal compound recovered in step (3), a fresh organometal compound may be used.

[0057]

With respect to the aromatic hydroxy compound used in step (4) of the method of the present invention, there is no particular limitation so long as it has a structure in which a hydroxy group is directly bonded to an aromatic group. The aromatic hydroxy compound used in step (4) is represented by the following formula (3):

$$ArOH \hspace{4cm} (3)$$

wherein Ar represents a C_5-C_{30} aromatic group.

[0058]

Examples of aromatic hydroxy compounds having an Ar group represented by formula (3) above include phenol; alkyl-

phenols, such as cresol (and isomers thereof), xylenol (and isomers thereof), trimethylphenol (and isomers thereof), tetramethylphenol (and isomers thereof), ethylphenol (and isomers thereof), propylphenol (and isomers thereof), butyl-phenol (and isomers thereof), diethylphenol (and isomers thereof), methylethylphenol (and isomers thereof), methylpro-pylphenol (and isomers thereof), dipropylphenol (and isomers thereof), methylbutylphenol (and isomers thereof), pentylphe-nol (and isomers thereof), hexylphenol (and isomers thereof) and cyclohexylphenol (and isomers thereof); alkoxyphenols, such as methoxyphenol (and isomers thereof) and ethoxyphenol (and isomers thereof); and substituted phenols represented by the below-mentioned formula (4):
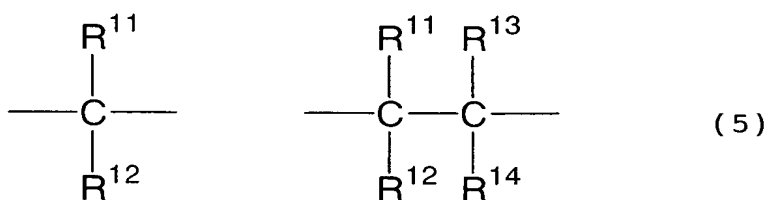
[0059]

(4)
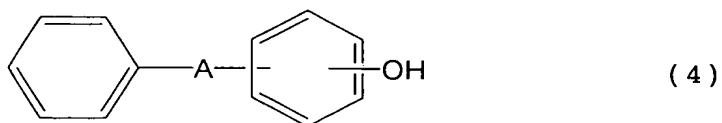
[0060]

wherein A represents a single bond; a divalent group, such as -O-, -S-, -CO- or -SO$_2$-; an unsub-stituted or substituted alkylene group represented by formula (5) below; or a cycloalkylene group rep-resented by formula (6) below,

wherein each of the aromatic rings may inde-
pendently be substituted with a lower alkyl group,
a lower alkoxy group, an ester group, a hydroxy
group, a nitro group, a halogen atom, a cyano group
or the like.

[0061]

$$-\overset{\displaystyle R^{11}}{\underset{\displaystyle R^{12}}{\overset{|}{\underset{|}{C}}}}- \qquad -\overset{\displaystyle R^{11}}{\underset{\displaystyle R^{12}}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle R^{13}}{\underset{\displaystyle R^{14}}{\overset{|}{\underset{|}{C}}}}- \qquad (5)$$

[0062]

wherein each of R^{11}, R^{12}, R^{13} and R^{14} independently
represents a hydrogen atom, a lower alkyl group, a
cycloalkyl group, an aryl group or an aralkyl group,
wherein each of the lower alkyl group, the cycloal-
kyl group, the aryl group and the aralkyl group is
optionally substituted with a halogen atom or an
alkoxy group.

[0063]

$$>\!C \underset{}{\overset{}{\frown}} (CH_2)_k \qquad (6)$$
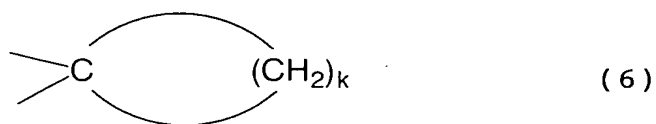
[0064]

wherein k is an integer of from 3 to 11, and each

hydrogen atom may be replaced by a lower alkyl

group, an aryl group or a halogen atom.

[0065]

Specific examples of aromatic hydroxy compounds repre-

sented by the above-mentioned formula (4) include naphthol

(and isomers thereof); substituted naphthols; and heteroaro-

matic hydroxy compounds, such as hydroxypiridine (and isomers

thereof), hydroxycoumarine (and isomers thereof) and

hydroxyquinoline (and isomers thereof).

Among the above-mentioned aromatic hydroxy compounds

represented by the above-mentioned formula (3), preferred are

aromatic hydroxy compounds having a C_6-C_{10} aromatic group as

the aromatic group Ar, and most preferred is phenol.

The type of the aromatic hydroxy compound used in the

present invention is appropriately selected depending on the

type of the desired aromatic carbonate. For example, when it

is desired to produce diphenyl carbonate, phenol is used as

the aromatic hydroxy compound; when it is desired to obtain

dicresyl carbonate, cresol is used as the aromatic hydroxy

compound; and when it is desired to produce dinaphthyl car-

bonate, naphthol is used as the aromatic hydroxy compound.

The aromatic hydroxy compound may have a substituent, such as

an alkyl group or a halogen atom. Further, the aromatic hydroxy compound may be a heterocyclic compound, such as hydroxypyridine.

[0066]

In step (4) of the method of the present invention, a component comprised mainly of the dialkyl carbonate separated in step (2) is reacted with an aromatic hydroxy compound to obtain an aromatic carbonate. With respect to methods in which a dialkyl carbonate is reacted with an aromatic hydroxy compound to obtain an alkyl aryl carbonate and a diaryl carbonate, there have conventionally been known a number of proposals. Such conventional methods can also be preferably used in the present invention.

In the present invention, the reaction performed in step (4) is a transesterification reaction between a dialkyl carbonate and an aromatic hydroxy compound. This reaction is an equilibrium reaction and, hence, for advancing the reaction, it is preferred that the reaction is performed while withdrawing a by-produced alcohol from the reaction system. From the viewpoint of efficiently withdrawing the by-produced alcohol, it is preferred that the aromatic hydroxy compound used in step (4) has a boiling point higher than that of the alcohol forming the dialkyl carbonate used in step (2). Es-

pecially, when the cycle of steps (1) to (4) is repeated at least one time, it is preferred that the alcohol has a boiling point lower than that of the aromatic hydroxy compound used in step (4). Specifically, it is preferred that the alcohol has a boiling point which is at least 2 °C lower than that of the aromatic hydroxy compound. Further, from the viewpoint of ease in the withdrawal of the by-produced alcohol in step (4), it is more preferred that the alcohol has a boiling point which is at least 10 °C lower than that of the aromatic hydroxy compound.

[0067]

Examples of dialkyl carbonates used in step (4) include dimethyl carbonate, diethyl carbonate, dipropyl carbonate (and isomers thereof), diallyl carbonate, dibutenyl carbonate (and isomers thereof), dibutyl carbonate (and isomers thereof), dipentyl carbonate (and isomers thereof), dihexyl carbonate (and isomers thereof), diheptyl carbonate (and isomers thereof), dioctyl carbonate (and isomers thereof), dinonyl carbonate (and isomers thereof), didecyl carbonate (and isomers thereof), dicyclopentyl carbonate, dicyclohexyl carbonate, dicycloheptyl carbonate, dibenzyl carbonate, diphenetyl carbonate (and isomers thereof), diphenylpropyl carbonate (and isomers thereof), diphenylbutyl carbonate (and

isomers thereof), dichlorobenzyl carbonate (and isomers thereof), dimethoxybenzyl carbonate (and isomers thereof), dimethoxymethyl carbonate, dimethoxyethyl carbonate (and isomers thereof), dichloroethyl carbonate (and isomers thereof), dicyanoethyl carbonate (and isomers thereof), methyl ethyl carbonate, methyl propyl carbonate (and isomers thereof), ethyl propyl carbonate (and isomers thereof), ethyl butyl carbonate (and isomers thereof), dibenzyl carbonate, ethylene carbonate and propylene carbonate. These dialkyl carbonates can be used individually or in combination.

[0068]

With respect to the dialkyl carbonate used in step (4), it is preferred that the alcohol forming the dialkyl carbonate has a boiling point higher than that of water. Among such alcohols, preferred are n-butyl alcohol, isobutyl alcohol, alkyl alcohols having a straight chain or branched C_5-C_{12} alkyl group, alkenyl alcohols having a straight chain or branched C_4-C_{12} alkenyl group, cycloalkyl alcohols and aralkyl alcohols. Further, from the viewpoint of withdrawing the by-produced alcohol from the reaction system in step (4) to thereby advance the reaction in step (4), it is more preferred that the boiling point of the alcohol is lower than that of the aromatic hydroxy compound used in step (4).

Therefore, it is preferred that the dialkyl carbonate used in
step (4) contains an alcohol having a boiling point higher
than that of water but lower than that of the aromatic hy-
droxy compound.

[0069]

Further, the same as explained above applies to the case
of the second alcohol used in step (1). Preferred examples
of second alcohols include alcohols having a straight chain
or branched alkyl group, such as n-butyl alcohol, isobutyl
alcohol, pentanol (and isomers thereof), hexanol (and isomers
thereof), heptanol (and isomers thereof), octanol (and iso-
mers thereof), nonyl alcohol (and isomers thereof), decyl al-
cohol (and isomers thereof), dodecyl alcohol (and isomers
thereof); and alcohols having a cycloalkyl group, such as
cyclobutanol, cyclopentanol and cyclohexanol. Further, when
the removal of water in step (3) is performed by distillation,
or when the reaction in step (4) is performed while withdraw-
ing the by-produced alcohol from the reaction system, it is
preferred that the second alcohol used in step (1) is a
straight chain or branched C_5-C_8 alkyl alcohol and a C_5-C_8
alicyclic alcohol.

[0070]

With respect to the above-mentioned alcohols, dialkyl

carbonate and aromatic hydroxy compound, it is most preferred that all of the first alcohol, the second alcohol, the alcohols corresponding to the alkoxy groups of the organometal compound (having a metal-carbon-oxygen linkage) represented by formula (1) or (2) above, and the alcohols forming the dialkyl carbonate are alcohols selected from the group consisting of pentanol (and isomers thereof) and hexanol (and isomers thereof); and that the aromatic hydroxy compound is selected from the group consisting of phenol and cresol.

[0071]

In step (4), the aromatic hydroxy compound is used in an amount which is 0.1 to 10,000 times the molar amount of the amount of the dialkyl carbonate which is separated in step (2) and used in step (4). The larger the amount of the aromatic hydroxy compound used, the larger the amount of an aromatic carbonate produced. However, when the amount of the aromatic hydroxy compound is too large, it becomes necessary to use a large reaction vessel. Further, since most of the reactions occurring in step (4) are equilibrium reactions, the use of too large an amount of the aromatic dihydroxy compound is disadvantageous in that, for recovering the aromatic carbonate produced, the use of a large distillation column becomes necessary. Therefore, in step (4), the amount of the

aromatic hydroxy compound is more preferably 1 to 1,000 times, most preferably 1 to 100 times, as large as the molar amount of the dialkyl carbonate.

In step (4), the dialkyl carbonate and the aromatic hydroxy compound are fed to the reaction vessel. If desired, a catalyst may also be used. An impurity may be present in the reaction system of step (4) so long as the impurity does not adversely affect the reactions in step (4).

[0072]

Each of the dialkyl carbonate and the aromatic hydroxy compound which are used as raw materials in step (4) may contain an alcohol, an alkyl aryl carbonate and a diaryl carbonate, which are products formed in step (4). However, the reaction for producing an alkyl aryl carbonate from the dialkyl carbonate and the aromatic hydroxy compound is a reversible reaction, so that, when the amounts of the above-mentioned products in the raw materials are large, there is a danger that the conversions of the raw materials are lowered. The amount ratio of the aromatic hydroxy compound to the dialkyl carbonate varies depending on the type and amount of a catalyst used and the reaction conditions; however, the amount ratio is preferably from 0.01 to 1,000, in terms of the molar ratio of the aromatic hydroxy compound to the dialkyl carbon-

ate.

[0073]

The time for the reaction in step (4) varies depending on the reaction conditions and the type and inner structure of the reaction vessel. However, the reaction time is generally from 0.001 to 50 hours, preferably from 0.01 to 10 hours, more preferably from 0.05 to 5 hours. The reaction temperature (i.e., temperature in the reaction vessel) varies depending on the types of the dialkyl carbonate and aromatic hydroxy compound used as raw materials. However, the reaction temperature is generally from 50 to 350 °C, preferably from 100 to 280 °C. The reaction pressure may be reduced pressure, atmospheric pressure or superatmospheric pressure, depending on the types of the dialkyl carbonate and aromatic hydroxy compound used as raw materials and the reaction temperature. However, the reaction pressure is generally from 10 Pa to 20 MPa.

[0074]

In step (4), it is not necessary to use a solvent. However, for facilitating the operations in step (4), there can be used an inert solvent. Examples of inert solvents include ethers, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated aliphatic hydrocarbons and halogenated aromatic hy-

drocarbons. Further, the reaction in step (4) may be performed in the presence of a gas inert to the reaction in step (4). Examples of such inert gases include nitrogen, helium, argon, and gasified, low boiling point organic compounds which are inert to the reaction in step (4). When step (4) is performed using a continuous multi-stage distillation column, for the purpose of promoting the removal of a low boiling point by-product by distillation, the above-mentioned inert gas or gasified, low boiling point organic compound may be introduced into the distillation column from the lower portion thereof.

[0075]

After completion of step (4), the aromatic carbonate is separated from the catalyst, the dialkyl carbonate, the aromatic hydroxy compound and the by-produced alcohol by a conventional method.

A catalyst may be used in step (4). As mentioned above, the reaction performed in step (4) is a transesterification reaction. By the transesterification reaction, an alkyl aryl carbonate and a diaryl carbonate are obtained from a dialkyl carbonate. However, the equilibrium of the transesterification reaction is biased in the direction of the original system and the rate of the reaction is low. Therefore, for im-

proving the method for producing an aromatic carbonate using the transesterification reaction, several methods have been proposed. Such improved methods can be preferably used in the present invention.

[0076]

With respect to the transesterification reaction catalyst, the amount thereof varies depending on the type of the catalyst, the type of the reaction vessel, the types and amounts of the dialkyl carbonate and aromatic hydroxy compound, and the reaction conditions (such as the reaction temperature and the reaction pressure). However, the amount of the catalyst is generally from 0.0001 to 50 % by weight, based on the total weight of the dialkyl carbonate and the aromatic hydroxy compound used as raw materials. When the catalyst is used in a solid form, it is preferred that the amount of the catalyst is from 0.01 to 75 % by volume, based on the inner volume of the empty reaction vessel.

[0077]

As catalysts for elevating the reaction rate, there are known a number of metal-containing catalysts. Conventional transesterification reaction catalysts can be used in the present invention. With respect to the transesterification reaction catalysts used in a method in which a dialkyl car-

bonate is reacted with an aromatic hydroxy compound to produce a reaction mixture containing an alkyl aryl carbonate and/or a diaryl carbonate, examples of such transesterification reaction catalysts include Lewis acids (such as transition metal halides) and compounds which generate Lewis acids (see Unexamined Japanese Patent Application Laid-Open Specification Nos. Sho 51-105032, Sho 56-123948 and Sho 56-123949 (corresponding to Unexamined West German Patent Application Laid-Open Specification No. 2528412, U.K. Patent No. 1499530 and U.S. Patent No. 4,182,726)); tin compounds, such as organotin alkoxides and organotin oxides (see Unexamined Japanese Patent Application Laid-Open Specification Nos. Sho 54-48733 (corresponding to Unexamined West German Patent Application Laid-Open Specification No. 2736062), Sho 54-63023, Sho 60-169444 (corresponding to U.S. Patent No. 4,554,110), Sho 60-169445 (corresponding to U.S. Patent No. 4,552,704), Sho 62-277345 and Hei 1-265063)); salts and alkoxides of an alkali metal or alkaline earth metal (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 57-176932); lead compounds (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 57-176932); complexes of a metal, such as copper, iron or zirconium (see Unexamined Japanese Patent Application Laid-Open Specification

No. Sho 57-183745); titanic esters (see Unexamined Japanese

Patent Application Laid-Open Specification No. Sho 58-185536

(corresponding to U.S. Patent No. 4,410,464)), mixtures of a

Lewis acid and a protonic acid (see Unexamined Japanese Pat-

ent Application Laid-Open Specification No. Sho 60-173016

(corresponding to U.S. Patent No. 4,609,501)); compounds of

Sc, Mo, Mn, Bi or Te (see Unexamined Japanese Patent Applica-

tion Laid-Open Specification No. Hei 1-265064); and ferric

acetate (see Unexamined Japanese Patent Application Laid-Open

Specification No. Sho 61-172852).

[0078]

In step (4), the reaction may be performed in the pres-

ence of not only a transesterification reaction catalyst but

also a disproportionation reaction catalyst. A number of dis-

proportionation reaction catalysts are known. Examples of

disproportionation reaction catalysts include Lewis acids and

transition metal compounds which generate Lewis acids (see

Unexamined Japanese Patent Application Laid-Open Specifica-

tion No. Sho 51-75044 (corresponding to Unexamined West Ger-

man Patent Application Laid-Open Specification No. 2552907

and U.S. Patent No. 4,045,464)); polymeric tin compounds (see

Unexamined Japanese Patent Application Laid-Open Specifica-

tion No. Sho 60-169444 (corresponding to U.S. Patent No.

4,554,110)); compounds represented by the formula: R-X(=O)OH (wherein X is Sn or Ti and R is a monovalent hydrocarbon group) (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-169445 (corresponding to U.S. Patent No. 4,552,704)); mixtures of a Lewis acid and a protonic acid (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-173016 (corresponding to U.S. Patent No. 4,609,501)); lead compounds (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-93560); compounds of titanium or zirconium (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-265062); tin compounds (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-265063); and compounds of Sc, Mo, Mn, Bi or Te (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-265064).

[0079]

With respect to the reaction performed in step (4) of the method of the present invention, it has been attempted to modify the reaction mode for displacing the equilibrium of the reaction in the direction of the desired product formation as much as possible, thereby improving the yield of an aromatic carbonate. For example, there have been proposed: a method in which methanol by-produced by the reaction of di-

methyl carbonate with phenol is distilled off in the form of
an azeotropic mixture thereof with an azeotrope former (see
Unexamined Japanese Patent Application Laid-Open Specifica-
tion Nos. Sho 54-48732 (corresponding to Unexamined West Ger-
man Patent Application Laid-Open Specification No. 736063 and
U.S. Patent No. 4,252,737) and Sho 61-291545); a method in
which methanol by-produced by the reaction of dimethyl car-
bonate with phenol is removed by adsorption thereof onto mo-
lecular sieves (see Unexamined Japanese Patent Application
Laid-Open Specification No. Sho 58-185536 (corresponding to
U.S. Patent No. 4,410,464)); a method in which an alcohol by-
produced by a transesterification reaction is distilled off
using a reaction vessel having attached to an upper potion
thereof a distillation column (see working examples of Unex-
amined Japanese Patent Application Laid-Open Specification No.
Sho 56-123948 (corresponding to U.S. Patent No. 4182726),
working examples of Unexamined Japanese Patent Application
Laid-Open Specification No. Sho 56-25138, working examples of
Unexamined Japanese Patent Application Laid-Open Specifica-
tion No. Sho 60-169444 (corresponding to U.S. Patent No.
4,554,110), working examples of Unexamined Japanese Patent
Application Laid-Open Specification No. Sho 60-169445 (corre-
sponding to U.S. Patent No. 4,552,704), working examples of

Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-173016 (corresponding to U.S. Patent No. 4,609,501), working examples of Unexamined Japanese Patent Application Laid-Open Specification No. Sho 61-172852, working examples of Unexamined Japanese Patent Application Laid-Open Specification No. Sho 61-291545, and working examples of Unexamined Japanese Patent Application Laid-Open Specification No. Sho 62-277345)); and a method in which a dialkyl carbonate and an aromatic hydroxy compound are continuously fed to a multi-stage distillation column to perform a reaction in the distillation column, wherein the reaction is continuously performed while continuously withdrawing a low boiling point mixture containing the by-produced alcohol by distillation and withdrawing a reaction mixture containing the produced alkyl aryl carbonate from a lower portion of the distillation column (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 3-291257). By any of the above-mentioned methods, a continuous production of an aromatic carbonate can be efficiently performed. Further examples of methods for continuously producing an aromatic carbonate include: a method in which a transesterification reaction is performed in the presence of a catalyst in a column type reaction vessel (see Unexamined Japanese Patent Applica-

tion Laid-Open Specification Nos. Hei 6-41022, Hei 6-157424

and Hei 6-184058); a method in which a plurality of reaction

vessels are connected in series (Unexamined Japanese Patent

Application Laid-Open Specification Nos. Hei 6-234707 and Hei

6-263694); a method using a bubble column reaction vessel

(Unexamined Japanese Patent Application Laid-Open Specifica-

tion No. Hei 6-298700); and a method using a vertical reac-

tion vessel (Unexamined Japanese Patent Application Laid-Open

Specification No. Hei 6-345697). In the commercial scale

production of an aromatic carbonate, it has also been at-

tempted to perform the production stably for a long period of

time. For example, in an attempt to prevent the deposition

of a catalyst in a distillation column, Unexamined Japanese

Patent Application Laid-Open Specification No. Hei 6-157410

proposes a method in which, in the production of an aromatic

carbonate from a dialkyl carbonate and an aromatic hydroxy

compound using a reaction vessel having attached thereto a

distillation column, an aliphatic alcohol by-produced is

withdrawn from the distillation column so that the concentra-

tion of the aliphatic alcohol in the reaction mixture in the

column is suppressed to 2 % by weight or less. This patent

document describes that the above-mentioned method enables a

stable practice of a continuous production of an aromatic

carbonate. Further, in an attempt to prevent the deposition of a catalyst in a distillation column for the purpose of stably producing an aromatic carbonate for a long period of time, Japanese Patent Application Prior-to-Examination Publication No. Hei 9-11049 discloses a method in which the amount of an aromatic polyhydroxy compound in the reaction mixture containing a catalyst is suppressed to 2 or less, in terms of the weight ratio of the aromatic polyhydroxy compound to the metal contained in the catalyst.

[0080]

It is known that, in the production of an aromatic carbonate from a dialkyl carbonate and an aromatic hydroxy compound, a compound having a high boiling point is by-produced. For example, Unexamined Japanese Patent Application Laid-Open Specification No. Sho 61-172852 describes that, in the production of diphenyl carbonate by the transesterification reaction of dimethyl carbonate with phenol, an impurity having a boiling point close to that of diphenyl carbonate is by-produced, and that the impurity gets mixed with the produced diphenyl carbonate, thereby leading to discoloration of the final product (such as a polycarbonate) obtained using the diphenyl carbonate. As an example of the impurity having a boiling point close to that of a diaryl carbonate (e.g., di-

phenyl carbonate), there can be mentioned an aryloxycarbonyl hydroxy arene, which is an isomer of a diaryl carbonate and is formed by the Fries rearrangement of a diaryl carbonate (such an example of an impurity is not described in the above-mentioned Unexamined Japanese Patent Application Laid-Open Specification No. Sho 61-172852). When diphenyl carbonate is used as the diaryl carbonate, the above-mentioned aryloxycarbonyl hydroxyl arene is phenyl salicylate, which has a high boiling point which is higher than that of diphenyl carbonate by 4 to 5 °C. When the reaction for producing an aromatic carbonate from a dialkyl carbonate and an aromatic hydroxy compound is performed for a long period of time, the above-mentioned high boiling point compound is gradually accumulated in the reaction system, so that the amount of the high boiling point compound contained in the aromatic carbonate produced is increased, thereby lowering the purity of the aromatic carbonate. Further, as the amount of the high boiling point compound contained in the reaction mixture increases, the boiling point of the reaction mixture is elevated, thereby posing a problem in that the by-production of the high boiling point compound is further promoted. On the other hand, however, by a method described in Unexamined Japanese Patent Application Laid-Open Specification No. Hei

11-92429, a high purity aromatic carbonate can be stably pro-

duced without the need for a large amount of the catalyst.

[0081]

The transesterification reaction catalysts used in the

present invention are those which accelerate the reactions of

formulae (7) and (8) above. Specific examples of trans-

esterification reaction catalysts include the following com-

pounds:

<lead compounds> lead oxides, such as PbO, PbO$_2$ and Pb$_3$O$_4$;

lead sulfides, such as PbS and Pb$_2$S; lead hydroxides, such as

Pb(OH)$_2$ and Pb$_2$O$_2$(OH)$_2$; plumbites, such as Na$_2$PbO$_2$, K$_2$PbO$_2$, NaH-

PbO$_2$ and KHPbO$_2$; plumbates, such as Na$_2$PbO$_3$, Na$_2$H$_2$PbO$_4$, K$_2$PbO$_3$,

K$_2$[Pb(OH)$_6$], K$_4$PbO$_4$, Ca$_2$PbO$_4$ and CaPbO$_3$; lead carbonates and ba-

sic salts thereof, such as PbCO$_3$ and 2PbCO$_3 \cdot$Pb(OH)$_2$; lead

salts of organic acids and basic salts of lead salts of or-

ganic acids, such as Pb(OCOCH$_3$)$_2$, Pb(OCOCH$_3$)$_4$, Pb(OCOCH$_3$)$_2 \cdot$

PbO$\cdot$3H$_2$O; organolead compounds, such as Bu$_4$Pb, Ph$_4$Pb, Bu$_3$PbCl,

Ph$_3$PbBr, Ph$_3$Pb (or Ph$_6$Pb$_2$), Bu$_3$PbOH and Ph$_3$PbO (wherein Bu

represents a butyl group and Ph represents a phenyl group);

lead alkoxides and lead aryloxides, such as Pb(OCH$_3$)$_2$,

(CH$_3$O)Pb(OPh) and Pb(OPh)$_2$; lead alloys, such as Pb-Na, Pb-Ca,

Pb-Ba, Pb-Sn and Pb-Sb; lead minerals, such as galena and

zinc blende; and hydration products of these lead compounds;

[0082]

<copper family metal compounds> copper family metal salts and complexes, such as CuCl, $CuCl_2$, CuBr, $CuBr_2$, CuI, CuI_2, $Cu(OAc)_2$, $Cu(acac)_2$, copper oleate, Bu_2Cu, $(CH_3O)_2Cu$, $AgNO_3$, AgBr, silver picrate, $AgC_6H_6ClO_4$, $Ag(bullvalene)_3NO_3$, $[AuC{\equiv}C-C(CH_3)_3]_n$ and $[Cu(C_7H_8)Cl]_4$ (wherein "acac" represents an acetylacetone chelate ligand);

<alkali metal complexes> alkali metal complexes, such as Li(acac) and $LiN(C_4H_9)_2$;

[0083]

<zinc complexes> zinc complexes, such as $Zn(acac)_2$;

<cadmium complexes> cadmium complexes, such as $Cd(acac)_2$;

<iron family metal compounds> iron family metal complexes, such as $Fe(C_{10}H_8)(CO)_5$, $Fe(CO)_5$, $Fe(C_4H_6)(CO)_3$, $Co(mesitylene)_2(PEt_2Ph)_2$, $CoC_5F_5(CO)_7$, $Ni-\pi-C_5H_5NO$ and ferrocene;

<zirconium complexes> zirconium complexes, such as $Zr(acac)_4$ and zirconocene;

<Lewis acid compounds> Lewis acids and transition metal compounds which generate Lewis acids, such as AlX_3, TiX_3, TiX_4, VOX_3, VX_5, ZnX_2, FeX_3 and SnX_4 (wherein X represents a halogen atom, an acetoxy group, an alkoxy group or an aryloxy group); and

[0084]

<organotin compounds> organotin compounds, such as

$(CH_3)_3SnOCOCH_3$, $(C_2H_5)_3SnOCOC_6H_5$, $Bu_3SnOCOCH_3$, $Ph_3SnOCOCH_3$,

$Bu_2Sn(OCOCH_3)_2$, $Bu_2Sn(OCOC_{11}H_{23})_2$, Ph_3SnOCH_3, $(C_2H_5)_3SnOPh$,

$Bu_2Sn(OCH_3)_2$, $Bu_2Sn(OC_2H_5)_2$, $Bu_2Sn(OPh)_2$, $Ph_2Sn(OCH_3)_2$,

$(C_2H_5)_3SnOH$, Ph_3SnOH, Bu_2SnO, $(C_8H_{17})_2SnO$, Bu_2SnCl_2 and $BuSnO(OH)$.

[0085]

Needless to say, each of the above-mentioned trans-
esterification reaction catalysts may be used in the form of
a reaction product thereof with an organic compound which is
present in the reaction system, such as an alcohol, an aro-
matic hydroxy compound, an alkyl aryl carbonate, a diaryl
carbonate or a dialkyl carbonate. Further, each of the
above-mentioned transesterification reaction catalysts may,
before the use thereof, be subjected to a heat treatment with
a raw material used in step (4) or with a product in step (4).

It is preferred that the transesterification reaction
catalyst has a high solubility in the reaction mixture under
the reaction conditions. Preferred examples of transesteri-
fication reaction catalysts include PbO, $Pb(OH)_2$ and $Pb(OPh)_2$;
$TiCl_4$ and $Ti(OPh)_4$; $SnCl_4$ and $Sn(OPh)_4$; Bu_2SnO and $Bu_2Sn(OPh)_2$;
$FeCl_3$, $Fe(OH)_3$ and $Fe(OPh)_3$; and compounds obtained by treat-
ing the above-mentioned compounds with phenol or the reaction

mixture.

[0086]

As mentioned above, in step (4), an aroamtic carbonate is produced by the transesterification reaction between a dialkyl carbonate and an aromatic hydroxy compound (this transesterification reaction is an equilibrium reaction). For displacing the equilibrium of the transesterification reaction in the direction of the desired product formation, it is preferred to perform the transesterification reaction while withdrawing a by-produced alcohol from the reaction system. The disproportionation reaction is also an equilibrium reaction. Therefore, when it is intended to obtain, as an aroamtic carbonate, a large amount of a diaryl carbonate, it is preferred to perform the disproportionation reaction while withdrawing one of the dialkyl carbonate and the diaryl carbonate (which are produced in the disproportionation reaction) from the reaction system. In the present invention, it is preferred that the alkoxy groups of the dialkyl carbonate produced is so selected that the dialkyl carbonate has a boiling point lower than that of the diaryl carbonate, and it is also preferred that the disproportionation reaction is performed while withdrawing the produced dialkyl carbonate from the reaction system.

[0087]

In step (4), the reaction may be performed in the presence of a disproportionation reaction catalyst as well as a transesterification reaction catalyst. Examples of disproportionation reaction catalysts include Lewis acids and transition metal compounds which generate Lewis acids (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 51-75044 (corresponding to Unexamined West German Patent Application Laid-Open Specification No. 2552907 and U.S. Patent No. 4,045,464)); polymeric tin compounds (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-169444 (corresponding to U.S. Patent No. 4,554,110)); compounds represented by the formula: R-X(=O)OH (wherein X is Sn or Ti and R is a monovalent hydrocarbon group) (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-169445 (corresponding to U.S. Patent No. 4,552,704)); mixtures of a Lewis acid and a protonic acid (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-173016 (corresponding to U.S. Patent No. 4,609,501)); lead compounds (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-93560); compounds of titanium or zirconium (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-265062); tin compounds (see Un-

examined Japanese Patent Application Laid-Open Specification No. Hei 1-265063)); and compounds of Sc, Mo, Mn, Bi or Te (see Unexamined Japanese Patent Application Laid-Open Specification No. Hei 1-265064).

[0088]

The disproportionation reaction catalysts used in the present invention are those which accelerate the reaction of formula (9) above. As disproportionation reaction catalysts, there can be mentioned transesterification reaction catalysts which can be used in step (4). Specific examples of disproportionation reaction catalysts include the following compounds:

<lead compounds> lead oxides, such as PbO, PbO_2 and Pb_3O_4; lead sulfides, such as PbS and Pb_2S; lead hydroxides, such as $Pb(OH)_2$ and $Pb_2O_2(OH)_2$; plumbites, such as Na_2PbO_2, K_2PbO_2, $NaHPbO_2$ and $KHPbO_2$; plumbates, such as Na_2PbO_3, $Na_2H_2PbO_4$, K_2PbO_3, $K_2[Pb(OH)_6]$, K_4PbO_4, Ca_2PbO_4 and $CaPbO_3$; lead carbonates and basic salts thereof, such as $PbCO_3$ and $2PbCO_3 \cdot Pb(OH)_2$; lead salts of organic acids and basic salts of lead salts of organic acids, such as $Pb(OCOCH_3)_2$, $Pb(OCOCH_3)_4$, $Pb(OCOCH_3)_2 \cdot PbO \cdot 3H_2O$; organolead compounds, such as Bu_4Pb, Ph_4Pb, Bu_3PbCl, Ph_3PbBr, Ph_3Pb (or Ph_6Pb_2), Bu_3PbOH and Ph_3PbO (wherein Bu represents a butyl group and Ph represents a phenyl group);

lead alkoxides and lead aryloxides, such as $Pb(OCH_3)_2$, $(CH_3O)Pb(OPh)$ and $Pb(OPh)_2$; lead alloys, such as Pb-Na, Pb-Ca, Pb-Ba, Pb-Sn and Pb-Sb; lead minerals, such as galena and zinc blende; and hydration products of these lead compounds;

[0089]

<copper family metal compounds> copper family metal salts and complexes, such as CuCl, $CuCl_2$, CuBr, $CuBr_2$, CuI, CuI_2, $Cu(OAc)_2$, $Cu(acac)_2$, copper oleate, Bu_2Cu, $(CH_3O)_2Cu$, $AgNO_3$, AgBr, silver picrate, $AgC_6H_6ClO_4$, $Ag(bullvalene)_3NO_3$, $[AuC\equiv C-C(CH_3)_3]_n$ and $[Cu(C_7H_8)Cl]_4$ (wherein "acac" represents an acetylacetone chelate ligand);

<alkali metal complexes> alkali metal complexes, such as $Li(acac)$ and $LiN(C_4H_9)_2$;

[0090]

<zinc complexes> zinc complexes, such as $Zn(acac)_2$;

<cadmium complexes> cadmium complexes, such as $Cd(acac)_2$;

<iron family metal compounds> iron family metal complexes, such as $Fe(C_{10}H_8)(CO)_5$, $Fe(CO)_5$, $Fe(C_4H_6)(CO)_3$, $Co(mesitylene)_2(PEt_2Ph)_2$, $CoC_5F_5(CO)_7$, $Ni-\pi-C_5H_5NO$ and ferrocene;

<zirconium complexes> zirconium complexes, such as $Zr(acac)_4$ and zirconocene;

<Lewis acid compounds> Lewis acids and transition metal com-

pounds which generate Lewis acids, such as AlX$_3$, TiX$_3$, TiX$_4$, VOX$_3$, VX$_5$, ZnX$_2$, FeX$_3$ and SnX$_4$ (wherein X represents a halogen atom, an acetoxy group, an alkoxy group or an aryloxy group); and

[0091]

<organotin compounds> organotin compounds, such as (CH$_3$)$_3$SnOCOCH$_3$, (C$_2$H$_5$)$_3$SnOCOC$_6$H$_5$, Bu$_3$SnOCOCH$_3$, Ph$_3$SnOCOCH$_3$, Bu$_2$Sn(OCOCH$_3$)$_2$, Bu$_2$Sn(OCOC$_{11}$H$_{23}$)$_2$, Ph$_3$SnOCH$_3$, (C$_2$H$_5$)$_3$SnOPh, Bu$_2$Sn(OCH$_3$)$_2$, Bu$_2$Sn(OC$_2$H$_5$)$_2$, Bu$_2$Sn(OPh)$_2$, Ph$_2$Sn(OCH$_3$)$_2$, (C$_2$H$_5$)$_3$SnOH, Ph$_3$SnOH, Bu$_2$SnO, (C$_8$H$_{17}$)$_2$SnO, Bu$_2$SnCl$_2$ and BuSnO(OH).

[0092]

Needless to say, each of the above-mentioned disproportionation (transesterification) reaction catalysts may be used in the form of a reaction product thereof with an organic compound which is present in the reaction system, such as an alcohol, an aromatic hydroxy compound, an alkyl aryl carbonate, a diaryl carbonate or a dialkyl carbonate. Further, each of the above-mentioned disproportionation (transesterification) reaction catalysts may, before the use thereof, be subjected to a heat treatment with a raw material used in step (4) or with a product in step (4).

It is preferred that the disproportionation (transesterification) reaction catalyst has a high solubility in

the reaction mixture under the reaction conditions. Pre-
ferred examples of disproportionation (transesterification)
reaction catalysts include PbO, Pb(OH)$_2$ and Pb(OPh)$_2$; TiCl$_4$
and Ti(OPh)$_4$; SnCl$_4$ and Sn(OPh)$_4$; Bu$_2$SnO and Bu$_2$Sn(OPh)$_2$; FeCl$_3$,
Fe(OH)$_3$ and Fe(OPh)$_3$; and compounds obtained by treating the
above-mentioned compounds with phenol or the reaction mixture.

[0093]

After completion of step (4), the aromatic carbonate is
separated from the catalyst, the aromatic hydroxy compound
and the alcohol by a conventional method to thereby recover
the aromatic carbonate.

With respect to the type of the reaction vessel used in
step (4), there is no particular limitation, and any conven-
tional reaction vessel can be used. Examples of conventional
reaction vessels include a stirring vessel, a multi-stage
stirring vessel, a multi-stage distillation column. These
reaction vessels can be used individually or in combination.
Using at least one of the above-mentioned reaction vessels,
step (4) may be performed in a batchwise or continuous manner.
From the viewpoint of efficiently displacing the equilibrium
of the reaction in the direction of the desired product for-
mation, it is preferred to use a multi-stage distillation
vessel. It is more preferred that step (4) is continuously

performed using a multi-stage distillation vessel. With re-

spect to the multi-stage distillation column, there is no

particular limitation so long as it is a distillation column

which has two or more theoretical stages and which is capable

of continuous distillation. As such a multi-stage distilla-

tion column, any conventional multi-stage distillation column

which is generally used in the art can be used. Examples of

such multi-stage distillation columns include a plate type

columns using a tray, such as a bubble-cap tray, a sieve tray,

a valve tray or a counterflow tray; and packed type columns

packed with various packings, such as a Raschig ring, a

Lesshing ring, a Pall ring, a Berl saddle, an Interlox saddle,

a Dixon packing, a McMahon packing, a Heli pack, a Sulzer

packing and Mellapak. Further, a mixed type of a plate col-

umn and packed column, which comprises both a plate portion

and a portion packed with packings, can also be preferably

used. When the production of a diaryl carbonate continuously

performed using a multi-stage distillation column, the pro-

duction is performed, for example, as follows. A starting

material and a reacting material are continuously fed to a

multi-stage distillation column to effect a transesterifica-

tion reaction between the starting material and the reacting

material in a liquid phase or a gaseous-liquid phase in the

presence of a metal-containing catalyst, thereby producing a reaction mixture containing an aromatic carbonate, wherein a high boiling point mixture containing the produced aromatic carbonate is withdrawn in a liquid form from a lower portion of the distillation column while continuously withdrawing, by distillation, a low boiling point mixture containing a by-product in a gaseous form from an upper portion of the distillation column.

[0094]

[Example]

Hereinbelow, the present invention will be described in more detail with reference to the following Example, which should not be construed as limiting the scope of the present invention.

<Measurements>

1)　Nuclear magnetic resonance (NMR) analysis of an organometal compound

Apparatus: JNM-A400 FT-NMR system (manufactured and sold by JEOL Ltd.)

(1)　Preparation of sample solutions for ^{1}H- and ^{13}C-NMR analyses

About 0.1 to 0.5 g of an organometal compound was weighed and, then, about 0.9 g of deuterated chloroform was

added thereto, thereby obtaining a sample solution for an NMR analysis.

(2) Preparation of a sample solution for a ^{119}Sn-NMR analysis

About 0.1 to 1 g of a liquid containing an organometal compound was weighed and, then, 0.05 g of tetramethyltin and about 0.85 g of deuterated chloroform were added thereto, thereby obtaining a sample solution for an NMR analysis.

[0095]

2) Gas chromatography (GC) analysis of a carbonic ester

Apparatus: GC-2010 system (manufactured and sold by Shimadzu Corporation).

(1) Preparation of a sample solution

0.06 g of a liquid to be measured with respect to the carbonic ester content thereof was weighed and, then, about 2.5 ml of dehydrated dimethylformamide or dehydrated acetonitrile was added thereto. Further, to the resultant was added about 0.06 g of diphenyl ether as an internal standard, thereby obtaining a sample solution for a GC analysis.

(2) Conditions for a GC analysis

Column: DB-1 (manufactured and sold by J & W Scientific)

Liquid phase: 100 % dimethyl polysiloxane

Column length: 30 m

Column diameter: 0.25 mm

Film thickness: 1 μm

Column temperature: the temperature was elevated from

50 °C to 300 °C at a rate of 10 °C/min.

Injection temperature: 300 °C

Detector temperature: 300 °C

Detector: FID (flame ionization detector)

(3) Quantitative analysis

The quantitative analysis of a sample solution was con-

ducted using a calibration curve obtained with respect to

standard samples.

[0096]

3) Calculation of the yield of a dialkyl carbonate

The yield of a dialkyl carbonate was expressed in terms

of the mol % of the dialkyl carbonate, based on the molar

amount of the metal atom contained in the organometal com-

pound used in step (1).

4) Calculation of the yield of an aromatic carbonate

The yields of an alkyl aryl carbonate and a diaryl car-

bonate were expressed in terms of the mol % of the alkyl aryl

carbonate and the diaryl carbonate, based on the molar amount

of the raw material (a dialkyl carbonate) used in step (4).

[0097]

[Example 1]

(Synthesis of dibutyltin di(3-methyl-1-butoxide))

Into a 1-liter four-neck flask equipped with a cooling tube (which was connected with a vacuum controller and a vacuum pump) and a Dean-Stark trap were charged 70.5 g (0.28 mol) of dibutyltin oxide (manufactured and sold by Aldrich), 502 g (5.7 mol) of 3-methyl-1-butanol (manufactured and sold by Aldrich). Further, a stirrer was placed in the flask. The flask was immersed in an oil bath having a temperature of 140 °C, and the pressure in the flask was gradually reduced to about 90 kPa while stirring the contents of the flask. Then, the pressure in the flask was further reduced to 85 kPa while stirring the contents of the flask and withdrawing a distillate from the flask, and a reaction was performed under 85 kPa for 12 hours while further withdrawing a distillate from the flask. Subsequently, unreacted components (such as an unreacted alcohol) in the flask were distilled off from the flask over 30 minutes while gradually reducing the pressure in the flask to about 200 Pa. The flask was taken out from the oil bath, and the inside of the flask was cooled. Then, nitrogen gas was introduced into the flask to elevate the pressure in the flask to atmospheric pressure. By this operation, 127 g of a viscous liquid was obtained. The distillate withdrawn from the flask was analyzed. As a result, it

was found that the distillate contained about 260 mmol of water. The above-obtained viscous liquid was analyzed by NMR. As a result, it was found that the viscous liquid contained dibutyltin di(3-methyl-1-butoxide) and 1,1,3,3-tetrabutyl-1,3-di(3-methyl-1-butoxy)distannoxane.

[0098]

(Step (1))

114 g of the above-obtained viscous liquid was charged into a 200-ml autoclave (manufactured and sold by Toyo Koatsu Co., Ltd.) which had a carbon dioxide gas bomb connected thereto through a SUS tube and a valve. The autoclave was sealed, and the atmosphere in the autoclave was purged with nitrogen gas. Then, the above-mentioned valve was opened to introduce carbon dioxide gas having a pressure thereof adjusted to 5 MPa into the autoclave. The introduction of carbon dioxide gas into the autoclave was performed for 10 minutes while stirring the contents of the autoclave, and, then, stopped by closing the valve of the carbon dioxide gas bomb. Subsequently, the internal temperature of the autoclave was elevated to 120 °C while stirring. Then, a reaction was performed for 4 hours while maintaining the internal pressure of the autoclave at about 4 MPa. During and after the reaction, samples of the reaction mixture in the autoclave were taken

and analyzed. As a result, it was found that the reaction mixture obtained 1 hour after the start of the reaction contained di(3-methyl-1-butyl) carbonate in an amount of 18 %, and that the reaction mixture obtained 4 hours after the start of the reaction (i.e., the reaction mixture after the reaction) contained di(3-methyl-1-butyl) carbonate in an amount of 20.4 %. After the reaction, the inside of the autoclave was cooled, and carbon dioxide was purged therefrom.

[0099]

(Step (2))

After step (1), the contents of the autoclave were cooled to room temperature (about 20 °C), and about 6 g of distilled water was charged into the autoclave, followed by stirring for 30 minutes, thereby performing a reaction. Then, the stirring was stopped and the autoclave was opened. It was found that a white slurry was obtained in the autoclave. The white slurry was subjected to filtration to thereby obtain white solids and a filtrate. The filtrate was charged into a 100-ml eggplant-shaped flask equipped with a cooling tube, a vacuum pump and a vacuum controller (manufactured and sold by Okano Works, Ltd.). Further, a stirrer was placed in the flask. Then, the flask was immersed in an oil bath having a temperature of 140 °C. A distillation was performed at

140 °C while stirring the contents of the flask and gradually reducing the pressure in the flask. During the distillation, water and 3-methyl-1-butanol were first distilled from the flask and, then, di(3-methyl-1-butyl) carbonate was distilled from the flask. The amount of the thus obtained di(3-methyl-1-butyl) carbonate was about 11 g.

[0100]

(Step (3))

Into a 1-liter four-neck flask equipped with a cooling tube (which was connected with a vacuum controller and a vacuum pump) and a Dean-Stark trap were charged the white solids obtained in step (2) above, 502 g (5.7 mol) of 3-methyl-1-butanol (manufactured and sold by Aldrich). Further, a stirrer was placed in the flask. The flask was immersed in an oil bath having a temperature of 140 °C, and the pressure in the flask was gradually reduced to about 90 kPa while stirring the contents of the flask. Then, the pressure in the flask was further reduced to 85 kPa while stirring the contents of the flask and withdrawing a distillate from the flask, and a reaction was performed under 85 kPa for 12 hours while further withdrawing a distillate from the flask. Thereafter, unreacted components (such as an unreacted alcohol) in the flask were removed from the flask over 30 minutes

while gradually reducing the pressure in the flask to about 200 Pa. The flask was taken out from the oil bath, and the inside of the flask was cooled. Then, nitrogen gas was introduced into the flask to elevate the pressure in the flask to atmospheric pressure. By this operation, 112 g of a viscous liquid was obtained. The above-obtained viscous liquid was analyzed by NMR. As a result, it was found that the viscous liquid contained dibutyltin di(3-methyl-1-butoxide) and 1,1,3,3-tetrabutyl-1,3-di(3-methyl-1-butoxy)distannoxane.

(Preparation of catalyst)

40 g of phenol and 8 g of lead monoxide were mixed together, and the resultant mixture was charged into a reaction vessel. Then, the mixture was heated at 180 °C for 10 hours while distilling off by-produced water with phenol, thereby obtaining catalyst A.

[0101]

(Step (4))

Into a 100-ml autoclave (manufactured and sold by Toyo Koatsu Co., Ltd.) were charged about 11 g of the di(3-methyl-1-butyl) carbonate obtained in step (2) above, 49 g of phenol (manufactured and sold by Aldrich) (which had been purified by distillation) and catalyst A obtained above, wherein the amount of catalyst A was such that the Pb content of the re-

sultant mixture in the autoclave became 0.4 % by weight.
Then, the autoclave was sealed, and a reaction between the
di(3-methyl-1-butyl) carbonate and the phenol was performed
as follows. The atmosphere in the autoclave was purged with
nitrogen gas. Then, all valves of the autoclave were closed,
and stirring of the contents of the autoclave was started.
In the autoclave, a reaction was performed as follows. The
internal temperature of the autoclave was elevated to 230 °C
while stirring the contents of the autoclave. Nitrogen gas
was introduced into the autoclave from the bottom thereof at
a rate of 50 ml/min while controlling the internal pressure
of the autoclave in the range of from 100 to 200 kPa by ap-
propriately operating a valve provided at an upper portion of
the autoclave, to thereby perform a distillation for about 4
hours to distill of a gaseous component from the autoclave.
Subsequently, the introduction of nitrogen into the autoclave
was stopped, and the resultant reaction mixture in the auto-
clave was allowed to cool. The reaction mixture in the auto-
clave was analyzed. As a result, it was found that the reac-
tion mixture contained about 28 mmol of di(3-methyl-1-butyl)
carbonate, about 21 mmol of 3-methyl-1-butyl phenyl carbonate
and about 2.6 mmol of diphenyl carbonate. The reaction mix-
ture in the autoclave was charged into a 100-ml three-neck

flask equipped with a cooling tube (which was connected with a vacuum controller and a vacuum pump) and a Dean-Stark trap. Further, a stirrer was placed in the flask. Then, the flask was immersed in an oil bath having a temperature of 150 °C. The pressure in the flask was gradually reduced to about 100 kPa while stirring the contents of the flask, thereby per-forming a reaction. During the reaction, unreacted phenol and di(3-methy-1-butyl) carbonate were distilled from the flask. The resultant liquid reaction mixture was comprised mainly of 3-methyl-1-butyl phenyl carbonate and diphenyl car-bonate.

[0102]

(Step (1) performed for the second time)

110 g of the viscous liquid obtained in step (3) above was charged into a 200-ml autoclave (manufactured and sold by Toyo Koatsu Co., Ltd.) which had a carbon dioxide gas bomb connected thereto through a SUS tube and a valve. The auto-clave was sealed, and the atmosphere in the autoclave was purged with nitrogen gas. Then, the above-mentioned valve was opened to introduce carbon dioxide gas having a pressure thereof adjusted to 5 MPa into the autoclave. The introduc-tion of carbon dioxide gas into the autoclave was performed for 10 minutes while stirring the contents of the autoclave,

and, then, stopped by closing the valve of the carbon dioxide gas bomb. Subsequently, the internal temperature of the autoclave was elevated to 120 °C while stirring. Then, a reaction was performed for 4 hours while maintaining the internal pressure of the autoclave at about 4 MPa. During and after the reaction, samples of the reaction mixture in the autoclave were taken and analyzed. As a result, it was found that the reaction mixture obtained 1 hour after the start of the reaction contained di(3-methyl-1-butyl) carbonate in an amount of 17 %, and that the reaction mixture obtained 4 hours after the start of the reaction (i.e., the reaction mixture after the reaction) contained di(3-methyl-1-butyl) carbonate in an amount of 21 %. After the reaction, the inside of the autoclave was cooled, and carbon dioxide was purged therefrom.

[0103]

[Effect of the Invention]

By the method of the present invention, an aromatic carbonate can be produced from an aromatic hydroxy compound and carbon dioxide having substantially no toxicity as a carbonyl source, without generating a large amount of a co-product or by-product. Therefore, the method of the present invention is very commercially advantageous.

[Name of Document] Abstract

[Abstract]

[Task] The task of the present invention is to provide a method for producing an aromatic carbonate using an organometal compound, an aromatic hydroxy compound and carbon dioxide.

[Means to Solve the Task] A method for producing an aromatic carbonate, comprising the steps of: (1) performing a reaction between an organometal compound and carbon dioxide in the presence of an alcohol to obtain a reaction mixture containing a carbonic ester, (2) separating the carbonic ester from the reaction mixture to obtain a residual liquid, (3) regenerating the organometal compound, and (4) obtaining an alkyl aryl carbonate.

[Selected Figure] None

[Name of Document]   Notification of Change of Applicant

                             (due to general succession)

[Date of Submission]   October 7, 2003

[Submitted to]   Commissioner, Japan Patent Office

[Designation of the Case]

    [Application Number] Patent Application No. 2003-185078

[Successor]

    [Identification Number] 303046314

    [Name]   Asahi Kasei Chemicals Corporation

    [Representative]   Taketsugu Fujiwara

[List of Materials Being Submitted]

    [Name of Material] Certified Copy of Commercial Regis-
tration 1

       [Designation of the Citation] Patent Application No.
Hei 03-046654

    [Name of Material] Certificate of Succession 1

       [Designation of the Citation] Patent Application No.
Hei 03-046654

Historical Information on Applicant

Identification Number   [000000033]

1.   Date of Change   January 4, 2001

      [Reason for Change]   Change of Name

      Address: 2-6, Dojimahama 1-chome, Kita-ku

                                Osaka-shi, Osaka

      Name: Asahi Kasei Kabushiki Kaisha

Historical Information on Applicant

Identification Number   [303046314]

1.   Date of Change   August 20, 2003

      [Reason for Change]   New Registration

      Address: 1-2, Yuraku-cho 1-chome,

                                 Chiyoda-ku, Tokyo

      Name: Asahi Kasei Chemicals

                                 Corporation